PHYSICAL SOCIETY OF LONDON

MEMOIRS

OF THE

COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

VOL. V, No. 2

DECEMBER 1921

KYOTO

The Spark Potential Difference between Spheres

By

Usaburo Yoshida

(Received April 25, 1921)

When a sufficiently large potential difference is applied between two metallic spheres the electric spark will pass between them. The maximum intensity of the electric field in front of one of the electrodes in this case was calculated by Schuster[1] and Russel[2] from the observed values of the spark potential between the electrodes. According to Schuster, the maximum electric intensity became smaller with the same electrode as the spark length was increased, and became larger with the same spark length as the diameter of the electrode was reduced. Next Russel arrived at a very simple conclusion that the maximum electric intensity in front of the electrode was independent of the spark length and the diameter of the electrode and attained to a value of about 38 kilovolts per centimetre in the air at ordinary pressure. He extended his calculation to the case of spark discharge between parallel cylindrical electrodes, and the same value for the maximum electric intensity was also found to be true in this case.

Now let V be the spark potential difference between two equal spherical electrodes, either of which is not grounded, then we may regard that the potential of one of the electrodes is V/2 and that of the other is $-V/2$. The spark potential V will be a function of the maximum electric field R_m in front of either of the electrodes, the radius of the electrode a and the shortest distance between the elec-

1 Schuster, Phil. Mag., **29**, 182, (1890).

2 Russel, Phil. Mag., **11**, 237, (1906).

trodes namely the spark length x. The actual relation of these quantities is given by Russel by the equation

$$V = R_m \frac{x}{f},$$

where f is a function of x/a as is shown numerically in the Table I.

When one of the electrodes is earthed, the intensity of the electric field is maximum just in front of the isolated sphere. In this case the relation between the maximum electric field and the potential difference between the electrodes is represented by a similar expression as before,

$$V = R_m \frac{x}{f_1},$$

where f_1 is also a function of x/a and its numerical value calculated by Schuster and Russel is shown in the Table I.

TABLE I.—Values of f and f_1

$\frac{x}{a}$	f	f_1	$\frac{x}{a}$	f	f_1
0.0	1.000	1.000	1.5	1.559	1.910
0.1	1.034	1.034	2.0	1.770	2.338
0.2	1.068	1.068	3.0	2.214	3.252
0.3	1.102	1.106	4.0	2.677	4.200
0.4	1.137	1.150	5.0	3.151	5.172
0.5	1.173	1.199	6.0	3.632	6.144
0.6	1.208	1.253	7.0	4.117	7.126
0.7	1.245	1.313	8.0	4.604	8.112
0.8	1.283	1.378	9.0	5.095	
0.9	1.321	1.446	10.0	5.586	
1.0	1.359	1.517	100.0	50.51	

Russel regarded the potential difference of 0.8 kilovolts, which was nearly equal to twice the minimum spark potential difference in the air, as the "lost volts" between the electrodes. The calculation of the maximum electric field in front of one of the electrodes was then carried on by assigning the spark potential difference minus the "lost volts" as the potential difference between the electrodes. The value of the maximum electric field obtained by Russel from the observed values of spark potential differences by many authors was nearly constant, and the mean value of 38 kilovolts per centimetre was given to the air at ordinary pressure as its "dielectric strength."

When, however, a wider range in the values of the spark length and the diameter of the electrode than those employed by Russel was considered, the maximum electric field in front of the electrode was no more constant as shown in Table II.

TABLE II.—Values of R_m in K. V. per c.m.

$\frac{x}{a}$	a=2.5 c.m.	a=1.0 c.m.	a=0.5 c.m.
0.5	36.7	—	—
1.0	38.2	40.9	—
2.0	40.1	41.8	46.3
4.0	—	43.6	47.1
5.0	—	44.8	46.9
6.0	—	—	48.6

Here the value of the maximum electric field R_m was calculated in the same way as Russel from the spark potential difference between two equal isolated spheres observed by Algermissen.[1]

In the calculation of the dielectric strength of a gas, made by Schuster and Russel, the effect of the presence of leading-in-wires was disregarded. But the experiment made by Paschen[2] indicated that the spark potential betweeen small spherical electrodes was somewhat higher with a thicker leading-in-wire than with a thinner one. Judging from this it might be inferred that the mere presence of a leading-in-wire, even though small, would have some influence upon the spark potential difference. As the mathematical calculation of this effect upon the spark potential between spheres seemed to be difficult, the writer attempted, for the present, to obtain an empirical formula showing the actual relation between the spark potential and the spark length for any value of the radius of the spherical electrode. The following formula (1) was found to express fairly well the Algermissen's value of the spark potential between two equal isolated spheres.

$$(1) \qquad V = 4 + 30 \times \frac{1 + 0.2\left(\frac{x}{a}\right)^{\frac{1}{2}}}{f},$$

where V was the spark potential difference between the electrodes expressed in kilovolt, and f a function of x/a as already shown in

1 Algermissen, Ann. d. Physik, **19**, 1007, (1906).

2 Paschen, Wied. Ann., **37**, 69, (1889).

Table I. The calculated spark potential difference and those observed by Algermissen are given in Table III, the agreement between them being very good.

TABLE III.

Spark potential in K. V., observed by Algermissen.

a=2.5 c.m.			a=1.0 c.m.			a=0.5 c.m.		
x in c.m.	Vcalc.	Vobs.	x in c.m.	Vcalc.	Vobs.	x in c.m.	Vcalc.	Vobs.
1.0	33.6	33.0	1	30.5	31.0	0.75	22.0	23.0
1.25	40.5	40.0	1.5	40.0	40.0	1.0	25.8	27.0
1.50	47.0	47.0	2.0	47.5	48.0	2.0	35 4	36.0
1.75	53.0	53.0	3.0	58.8	59.0	3.0	40.9	41.0
2.00	59.4	59.0	4.0	66.9	66.0	4.0	44.9	44.0
2.50	70.3	70.5	5.0	72.9	72.0	4.5	46.5	45.0
3.75	94.0	94.0	5.5	75.8	74.5	5.0	47.8	46 5
4.50	106.1	107.0						

For Heydweiller's[1] value of the spark potential between two equal isolated spheres the same formula as before was seen also to hold good for the most part of the spark lengths except for very short ones, and the calculated values came out somewhat larger than observed ones for the very short sparks as shown in Table IV.

TABLE IV.

Spark potential in K. V., observed by Heydweiller.

a=2.5 c.m.			a=1 0 c.m.			a=0 5 c.m.		
x in c.m.	Vcalc.	Vobs.	x in c.m.	Vcalc.	Vobs.	x in c.m.	Vcalc.	Vobs.
0.5	19.3	18.4	0.1	7.1	4.7	0.1	7.1	4.8
0.6	22.3	21.6	0.2	10.1	8.1	0.2	9.9	8.4
0.7	25.2	24.5	0.4	15.9	14.5	0.3	12.6	11.4
0.8	28.1	27.3	0.6	21.2	20.4	0.4	15.1	14.6
0 9	30.8	30.1	0.8	26.2	26.1	0.5	17.2	17.3
1.0	33.7	32.8	1.0	30.4	31.3	0 6	19 2	20.0
1.2	39.2	38.2	1.2	34.5	35.5	0.7	21.1	22.1
1.4	44.4	43.6	1.4	38.1	38.7	0.8	22.8	24.1
1.6	49.7	48.8	1.6	41.6	41.2	1.0	25.7	27.0

[1] Heydweiller, Wied. Ann., **48**, 213, (1893).

Baille's[1] observation on the spark potential between two equal spheres, one charged and insulated and the other earthed, is again formulated in the similar manner as before, but with f_1 instead of f as given in the following equation.

$$(2) \qquad V = 5 + 98.5 \times \frac{1 + 0.297(\frac{x}{a})^{\frac{1}{2}}}{f_1},$$

where V represents the spark potential in electrostatic units. The calculated and the observed values are compared in Table V, and it may be seen from this table that the discrepancy between the calculated and the observed values is within the limit of experimental errors.

TABLE V.

Spark potential V in C.G.S.E.S.U., observed by Baille.

	x in c.m.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$a=3$ c.m.	Vcalc.	15.2	25.6	36.3	46.8	57.6	67.6	78.0	88.1	98.0	108.9
	Vobs.	14.8	25.6	36.1	46.3	55.1	65.2	75.4	88.0	97.4	112.9
	x in c.m.	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$a=1.5$ c.m.	Vcalc.	15.4	25.9	36.1	46.5	56.1	66.1	74.9	84.1	93.0	99.6
	Vobs.	15.0	26.0	36.6	45.9	55.0	65.2	73.8	84.8	94.6	104.7

Paschen[2] and Orgler[3] measured the spark potential difference between two equal spheres, one being earthed, in some gases under various pressures below the atmospheric one. Orgler experimented on the gases air, hydrogen, carbon dioxide, nitrogen and oxygen with the spherical electrodes of radius 1.25 c.m. His result may be represented by the following equation (3) throughout all ranges of spark lengths and pressures, and for every kind of gases.

$$(3) \qquad V = C + R_m \times \frac{1 + 0.46(\frac{x}{a})^{\frac{1}{2}}}{f_1},$$

1 Baille, J. J. Thomson, Conduction of Electricity through Gases, 461, (1906).

2 Paschen, Wied. Ann., **37**, 69, (1889).

3 Orgler, Ann. d. Physik, **1**, 159, (1900).

where C and R_m are independent of the spark length as in the former cases, and they depend only on the pressure and the nature of the gas. Their numerical values corresponding to each kind of gases and various values of its pressure are given in the Table XI. And in the tables from Table VI to X the values of the spark potential difference observed and calculated by the equation (3) are tabulated. The coincidence between them is within the limit of experimental errors.

TABLE VI.

Air, a=1.25 c.m., V in C.G.S.E.S.U., p the pressure in c.m. of mercury, observed by Orgler.

x in c.m.		0.04	0.06	0.08	0.1	0.2	0.3	0.4	0.5
p=75	Vcalc.	8.1	10.3	12.5	14.8	26.4	37.7	49.0	59.9
c=3.8									
R_m=100.0	Vobs.	7.5	10.1	12.7	15.2	27.3	38.6	48.8	58.2
p=55	Vcalc.	6.7	8.3	10.0	11.7	20.5	29.1	37.8	45.3
c=3.3									
R_m=76.4	Vobs.	6.1	8.1	10.1	12.0	21.3	29.8	37.6	44.9
p=35	Vcalc.	4.9	6.1	7.2	8.5	14.5	20.4	26.4	32.1
c=2.7									
R_m=52.2	Vobs.	4.6	6.1	7.4	8.7	15.0	20.9	26.2	31.1
p=15	Vcalc.		3.8	4.3	4.9	7.9	10.8	13.7	16.5
c=2.1									
R_m=25.6	Vobs.		3.5	4.3	5.0	8.2	11.0	13.6	16.2
p=10	Vcalc.		2.74	3.17	3.61	5.83	8.00	10.15	12.28
c=1.5									
R_m=19.2	Vobs.		2.57	3.10	3.64	6.13	8.16	10.05	11.93
p=6	Vcalc.		2.06	2.35	2.65	4.17	5.68	7.17	8.60
c=1.20									
R_m=13.2	Vobs.		1.94	2.30	2.65	4.31	5.80	7.13	8.35
p=4	Vcalc.		1.69	1.90	2.13	3.27	4.39	5.49	6.56
c=1.05									
R_m=9.82	Vobs.		1.61	1.89	2.16	3.39	4.50	5.48	6.38

TABLE VII.

Carbon dioxide, $a=1.25$ c.m., V in C.G.S.E.S.U., p the pressure in c.m. of mercury, observed by Orgler.

x in c.m.		0.04	0.06	0.08	0.1	0.2	0.3	0.4	0.5	0.6
p=75	Vcalc.	8.4	10.3	12.2	14.1	24.1	33.8	43.5	52.8	62.0
c=4.7										
R_m=85.7	Vobs.	8.0	10.2	12.4	14.5	24.8	34.7	43.9	52.4	60.5
p=55	Vcalc.	7.2	8.7	10.2	11.7	19.3	26.8	34.2	41.5	48.6
c=4.4										
R_m=66.1	Vobs.	6.7	8.5	10.2	11.9	20.1	27.6	34.5	41.1	47.4
p=35	Vcalc.	5.6	6.5	7.5	8.6	13.8	19.0	24.1	29.0	33.8
c=3.6										
R_m=45.2	Vobs.	5.2	6.5	7.7	8.9	14.4	19.6	24.3	28.8	33.1
p=15	Vcalc.		4.45	4.94	5.45	8.03	10.58	13.08	15.55	17.95
c=3.0										
R_m=22.3	Vobs.		4.13	4.79	5.42	8.29	10.80	13.18	15.52	17.85
p=10	Vcalc.		3.57	3.93	4.31	6.21	8.08	9.94	11.74	13.50
c=2.5										
R_m=16.4	Vobs.		3.28	3.77	4.25	6.50	8.35	10.09	11.79	13.40
p=6	Vcalc.			3.08	3.34	4.63	5.90	7.17	8.40	9.60
c=2.1										
R_m=11.2	Vobs.			3.00	3.34	4.78	6.11	7.29	8.40	9.54

TABLE VIII.

Hydrogen, $a=1.25$ c.m., V in C.G.S.E.S.U., p the pressure in c.m. of mercury, observed by Orgler.

x in c.m.		0.05	0.08	0.1	0.2	0.3	0.5	0.6
p=75	Vcalc.	6.3	8.0	9.2	15.4	21.4	33.1	39.8
c=3.4								
K_m=53.0	Vobs.	5.5	7.8	9.2	15.9	22.0	32.9	37.5
p=55	Vcalc.	5.0	6.4	7.3	12.1	16.7	25.9	30.2
c=2.8								
R_m=41.1	Vobs.	4.6	6.3	7.4	12.6	17.4	25.7	29.3
p=35	Vcalc.	3.66	4.60	5.26	8.60	11.85	18.25	21.30
c=2.1								
R_m=28.7	Vobs.	3.48	4.62	5.38	8.98	12.37	18.23	20.72
p=15	Vcalc.	2.47	2.94	3.26	4.90	6.52	9.68	11.20
c=1.7								
R_m=14 2	Vobs.	2.27	2.91	3.31	5.11	6.60	9.57	11.01
p=10	Vcalc.	1.87	2.22	2.46	3.68	4.88	7.22	8.34
c=1.3								
R_m=10.55	Vobs.	1.78	2.25	2.54	3.86	4.99	7.16	8.28
p=6	Vcalc.			2.07	2,87	3.66	5.19	5.93
c=1.31								
R_m=6.91	Vobs.			2.01	2.90	3.73	5.18	5.90

TABLE IX.

Nitrogen, $a=1.25$ c.m., V in C.G.S.E.S.U., p the pressure in c.m. of mercury, observed by Orgler.

x in c.m.		0.06	0.1	0.2	0.3	0.5
p=75 c=4.8 R_m=101.4	Vcalc.	11.4	16.0	27.7	39.2	61.8
	Vobs.	10.9	16.3	28.7	40.0	60.4
p=55 c=4.0 R_m=78.7	Vcalc.	9.1	12.7	21.8	30.7	49.2
	Vobs.	8.8	13.1	23.0	31.6	47.3
p=35 c=3.5 R_m=54.3	Vcalc.	6.5	9.5	15.8	21.9	34.0
	Vobs.	6.6	9.5	16.1	22.3	33.2
p=15 c=2.3 R_m=27.2	Vcalc.	4.1	5.3	8.5	11.6	17.6
	Vobs.	3.9	5.4	8.7	11.7	17.3
p=10 c=2.10 R_m=19.40	Vcalc.		4.23	6.47	8.68	13.00
	Vobs.		4.06	6.62	8.82	12.80

TABLE X.

Oxygen, $a=1.25$ c.m., V in C.G.S.E.S.U., p the pressure in c.m. of mercury, observed by Orgler.

x in c.m.		0.06	0.1	0.2	0.3	0.5
p=75 c=3.8 R_m=88.0	Vcalc.	9.5	13.5	23.6	33.6	53.3
	Vobs.	9.2	13.6	24.1	34.3	52.3
p=55 c=3.4 R_m=67,3	Vcalc.	7.8	10.8	18.6	26.2	41.2
	Vobs.	7.4	11.0	19.0	26.7	40.5
p=35 c=2.85 R_m=45.3	Vcalc.	5.80	7.83	13.07	18.25	28.35
	Vobs.	5.54	7.95	13.42	18.62	27.75
p=15 c=2.0 R_m=22.6	Vcalc.	3.46	4.48	7.10	9.65	14.65
	Vobs.	3.30	4.53	7.40	9.81	14.40
p=10 c=1.86 R_m=15.7	Vcalc.		3.59	5.41	7.19	10.69
	Vobs.		3.42	5.58	7.32	10.57

TABLE XI.

Orgler, $a = 1.25$ c.m., the values of C and R_m, p the pressure in c.m. of mercury.

p	Air		H_2		CO_2		N_2		O_2	
	C	R_m	C	R_m	C	R_m	C	R_m	C	R_m
4	1.05	9.82								
6	1.2	13.2	1.31	6 91	2.10	11.2	2.0	12.5	1.60	10.55
10	1.5	19.2	1.3	10.55	2.5	16.4	2.1	19.4	1.86	15.7
15	2.1	25.6	1.7	14 2	3.0	22.3	2.3	27.2	2.0	22.6
25	2.2	39.6	1.7	21.75	3.3	34.8	2.9	41.0	2.4	34.4
35	2 7	52.2	2.1	28.7	3.6	45.2	3.5	54.3	2.85	45.3
45	3.1	64.3	2.4	35.2	4.0	55.8	3.8	66.5	3.1	56.2
55	3.3	76.4	2.8	41.1	4.4	66 1	4.0	78.7	3.4	67.3
65	3.4	88.5	2.9	47.25	4.7	75.5	4.6	90.1	3.5	78.3
75	3.8	100.0	3.4	53.0	4.7	85.7	4.8	101.4	3.8	88.0

Paschen's experiment was made on air, hydrogen and carbon dioxide with the spherical electrodes of radius 1 c.m. His result is also represented by a similar equation as (3), but with a somewhat different constants as shown in the following equation (4).

$$(4) \qquad V = C + R_m \times \frac{1 + 0.356\left(\frac{x}{a}\right)^{\frac{1}{2}}}{f_1}.$$

The values of C and R_m, which were so determined as to fit the Paschen's observation, are given in Table XII. The spark potentials calculated by the equation (4) assigning proper values to C and R_m, as given in Table XII, are seen to be in fair agreement with the observed values. The values of R_m for gases at different pressures obtained from the experiments of Orgler and Paschen are plotted in Fig. 1.

Here it must be especially remarked that the expressions $\{1 + 0.46\left(\frac{x}{a}\right)^{\frac{1}{2}}\}/f_1$ and $\{1 + 0.356\left(\frac{x}{a}\right)^{\frac{1}{2}}\}/f_1$ in the equations (3) and (4) corresponding to the observation of Orgler and Paschen respectively are independent of the pressure and the nature of the gas.

For sparks, which are not very short, between parallel plates the relation between the spark potential and the spark length is a linear one. If V is the spark potential measured in electrostatic units and

x the spark length at atmospheric pressure measured in centimeters, then

$$V = C + R_m x. \tag{5}$$

The values of C and R_m obtained from the experiments made by Baille[1] anc Liebig[2] are given in Table XIII.

TABLE XII.

Paschen, $a = 1$ c.m., the values of C and R_m, p the pressure in c.m. of mercury.

p	Air		H_2		CO_2	
	C	R_m	C	R_m	C	R_m
2	1.68	5.58	1.1	3.03	2.6	5.14
6	1.80	13 00	1.7	7.0	3.2	12.0
10	2.70	18.57	1 9	10.33	4.2	16.2
20	4.0	31.5	2.3	18.0	6.1	26.8
30	4.5	44.9	2.8	24.8	7,1	37.8
40	5.1	57.5	3.2	31.4	8.1	48.0
50	5.3	66.9	3.7	37.5	8.1	59.9
60	5.7	81.8	4.2	43.5	8.4	70.8
70	—	—	4.9	49.0	8.8	80.9
75	6.6	98.3	4.8	52.3	9.0	85.6

TABLE XIII.

	Air		H_2		CO_2	
	C	R_m	C	R_m	C	R_m
Baille	5.0	99.6	—	—	—	—
Liebig	7.7	100.5	11.0	53.0	12.0	90.0

All the expressions from (1) to (4) may be extended to the case of sparks between parallel planes, by making the value of the radius a of the electrode infinite. Thus putting x/a equal to zero and f, f_1

1 Baille, loc. cit.

2 Liebig, Phil. Mag., **24**, 106, (1887).

each equal to 1, all these expressions take the form given in (5). If the spark potential is represented in electrostatic units, and the spark length in centimeter, the constants C and R_m thus obtained for gases at atmospheric pressure take the values shown in Table XIV.

TABLE XIV.

	Air		H_2		CO_2		N_2		O_2	
	C	R_m	C	R_m	C	R_m	C	R_m	C	R_m
Algermissen and Heydweiller ...	13.3	100.0								
Baille	5.0	98.5								
Orgler	3.8	100.0	3.4	53.0	4.7	85.7	4.8	101 4	3.8	88.0
Paschen	6.6	98.3	4.8	52.3	9.0	85.6	—	—	—	—
Mean	7.1	99.2	4.1	52.7	6.9	85.7	4.8	101.4	3.8	88.0

In this table, the numerical values of C and R_m for Algermissen's and Heydweiller's experiments are taken from the equation (1), and those for Baille are taken from the equation (2); and those for Orgler's and Paschen's experiments the values at the pressure of 75 c.m.s of mercury as shown in Table XI and XII. The values of R_m for a gas shown in Table XIV are in fair agreement to each other, and they are also equal to those given in Table XIII, where they were deduced from the observations on the spark potentials between two nearly parallel plates. As to the values of C, we notice that they differ from each other by a pretty amount. This may possibly due to some unknown causes. But, as this value of C is small compared with the total spark potential, it is very difficult to determine its value accurately. Thus we may conclude that the value deduced from the experiments of different authors is, at least, of the same order of magnitude.

The spark potential difference between two parallel plates increases linearly with the spark length but not proportionally, on account of the constant term C as stated before. Perhaps this may be due to the fact that there is a certain special difference of potential between the electrode and the gas just in contact with it, somewhat similar to the anode or cathode fall of potential in the case of vacuum discharges. This special difference of potential between the electrode and the gas

just in contact with it would perhaps be caused by the accumulation of ions generated in the gas by the preliminary ionisation in the stage of the so-called "lag" of the spark. If we interpret the constant term C in such a way, the meaning of the other constant $R_m = dV/dx$ becomes now clear; indeed it represents the intensity of the electric field in the gas when the spark discharge just occurs and it may be termed "the dielectric strength" of the gas as was commonly called.

It was already stated that, in the case of the spark discharge between spheres, the spark potential can be represented by a general formula of the following type:—

$$V - C = R_m \times \frac{1 + \alpha\left(\frac{x}{a}\right)^{\frac{1}{2}}}{f'} \tag{6}$$

where C, R_m and α are constants and f' represents either f or f_1 which are the functions of $\frac{a}{x}$ and correspond respectively to the case of the two isolatad electrodes and the case of the one electrode earthed. If we assume that the constant term C is the potential difference between the electrode and the gas just in contact with it, and that, as the ideal case, the spherical electrodes have no leading-in-wire, then the relation between the spark potential V and the maximum electric field R_m in the gas beyond the region of the cathode or anode fall of potential is connected by the expression

$$V - C = R_m \frac{x}{f'}. \tag{7}$$

When the right hand member of this equation is multiplied by the factor $1 + \alpha\left(\frac{x}{a}\right)^{\frac{1}{2}}$, the equation becomes identical to the formula (6). It was already stated that the constant α in this factor was independent of the pressure and the nature of the gas. Thus considering it seems not to be absurd to imagine that the above factor is a correction to be applied to $1/f'$ in the equation (7) in virtue of the presence of leading-in-wires and some other bodies in the neighborhood of the spark gap.

If this consideration is allowed, the constant R_m in the empirical formula (6) will have the same meaning as that in the equation (7) and it will represent the maximum electric field in the gas beyond the region of the cathode or anode fall of potential; and this important constant may be called "the dielectric strength" of the gas.

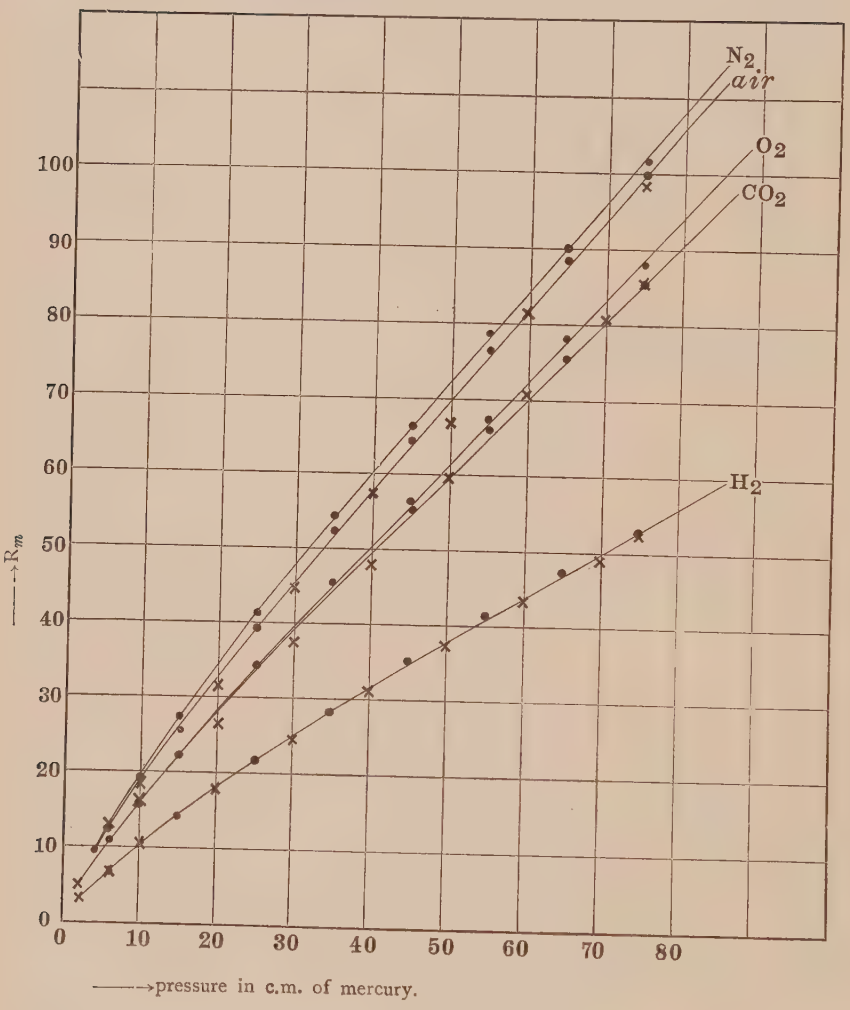
Under such consideration, the spark discharge seems to occur

between spheres when there is a certain amount of potential fall between the electrode and the gas just in contact with it perhaps due to the accumulation of ions toward the electrodes, and when the intensity of the electric field in the gas just beyond this region of the cathode or anode fall of potential has attained to a certain value characteristic to the pressure and the nature of the gas. When once the electric field of this kind was established between the electrodes, the brush discharge would start and grow from either of the two electrodes or from the both simultaneously; and the spark will pass, at last, across the electrodes along the path made by the brush discharge.

In conclusion the writer wishes to express his hearty thanks to Prof. Mizuno for his interest in the research.

Fig. 1.

• Observed by Orgler, Table XI.
× Observed by Paschen, Table XII.



Electrolytic Reactions of Naphthalene and its Derivatives. Part I.

Electrolytic Oxidation of Naphthalene

By

Kashichi Ono

(Received May 2, 1921)

A. Panchaud de Bottens[1] obtained, by the electrolytic oxidation of naphthalene, a small quantity of α-naphthoquinone and a brown oxidation product of an unknown composition when he used sulphuric acid-acetone solution with platinum and lead electrodes, while he obtained a very small quantity of phthalic acid by using sulphuric acid-acetic acid solution with platinum electrodes. There is apparently no record in chemical literature of the details of the progress of this electrolytic oxidation and the influence of the external conditions upon the reaction.

I have undertaken, in the detailed investigation reported in the present paper, to clear up the true nature of the electrolytic oxidation of naphthalene and its derivatives by studying, above all, the influence of the concentration of sulphuric acid, the current density, the temperature, the nature of the oxygen-carrier and of the solvent, etc., upon the process of the oxidation reaction.

According to my experiments, the electrolytic oxidation of naphthalene takes place only in an acid (sulphuric acid-acetone or sulphuric acid-acetic acid) solution; in an alkaline solution (50 c.c. of 20% sodium hydroxide, 100 c.c. of acetone and 3.8 grams naphthalene with platinum electrodes) no appreciable reaction is observed. The yield

of α-naphthoquinone and the oxidation efficiency is greater in a sulphuric acid-acetone solution than in a sulphuric acid-acetic acid solution. As the anode material, platinum, lead-peroxide, nickel, lead and iron were used, of which lead-peroxide or platinum gave the best results (Table I). This is due to the higher overvoltage of oxygen evolution, and, especially in the case of lead-peroxide, to its catalytic action as maintained by Müller and Soller.[2] The most suitable concentration of sulphuric acid is obtained when it is mixed in the proportion of 20–30 c.c. of sulphuric acid (sp. gr. 1.84) to 100 c.c. of water (Table 2, 3 and 11). I found that the greater the current density is, the higher the oxidation efficiency becomes, but that the production of α-naphthoquinone with lead-peroxide electrode is greatest at about 2 amp./100 cm.^{2} (Table 4), while with platinum electrode it is greatest at about 3 amp./100 cm.^{2} (Table 5 and 12). The elevation of the electrolytic temperature always increases the oxidation efficiency, but the production of α-naphthoquinone does not necessarily go parallel with the elevation of the temperature, and with the lead-peroxide electrode it is found to be better at the room temperature (Table 6). But with the platinum electrode the elevation of temperature and the production of α-naphthoquinone run parallel (Table 7). At the beginning of this investigation it was expected that a great quantity of α-naphthoquinone would be prepared by this electrolytic oxidation reaction; but it was soon found that α-naphthoquinone once produced is not only further oxidized into phthalic acid, but is also polimerised into a dark brown substance. As it is evident from Table 8, the increase of the current quantity is accompanied by the decrease of α-naphthoquinone and this is evidently due to the faster increase of the side reaction than that of the formation of α-naphthoquinone.

When a substance, which is easily oxidized by the electric current in the electrolytic oxidation reaction, and is changed into a strong oxidizing agent, is added into the solution of the electrolyte, the oxidation efficiency is made remarkably higher by the catalytic action. As the catalysers of this stamp, the salts of cerium, vanadium, chromium, manganese, ferrocyanides and chlorates are generally used.[3]

There are patents for using cerium,[4] vanadium[5] and chromium[6] compounds as oxygen-carriers in the electrolytic oxidation of naphthalene.

I have found the following substances to be effective in the order given:—Cerium nitrate, vanadic acid, potassium chlorate, potassium

chromate, manganese sulphate, potassium ferrocyanide, chrome-alum, etc. (Table 9, 10 and 13).

It is already known that naphthalene gives first α-naphthoquinone and then phthalonic acid and at last phthalic acid by the pure chemical oxidation[7] reaction. In my preliminary experiment I obtained among the products, α-naphthoquinone and phthalic acid. This fact induces me to assume that the same steps are followed in the electrolytic oxidation of naphthalene as in the purely chemical oxidation. The only question is whether α-naphthoquinone is directly produced by the oxidation of naphthalene without any intermediate product. In the degree of oxidation, quinones may be considered to be in a similar stage as ketones and aldehydes. A quinone may be, therefore, expected to be obtained by the oxidation of a phenolic compound, as ketones and aldehydes are produced by the oxidation of alcohols. R. Leeds[8] has already observed that the aromatic compounds are transformed into the hydroxy-derivatives by the purely chemical oxidation. He has thus obtained phenol from benzene and naphthol from naphthalene. It has been also shown that by the electrolytic oxidation of benzene, phenol[9] and benzoic acid,[10] there are produced catechol and 2-5-dihydroxy-benzoic acid, etc.

By the colour reaction toward ferric chloride and bleaching powder I have qualitatively confirmed the presence of α-naphthol in the electrolytic solution as the intermediate product of the oxidation. By the steam distillation of the products of the electrolytic oxidation of naphthalene, a red substance is obtained which is presumably identical with the compound of α-naphthol and α-naphthoquinone obtainable by the electrolytic oxidation of α-naphthol. Thus it appears natural to conclude that naphthalene is oxidized at the first stage into α-naphthol.

In all my experiments I have found that a considerable quantity of a dark brown resinous substance was produced. A. Panchaud de Bottens[1] recognized the same substance and tried in vain to reduce it with phosphorus and hydroiodic acid in order to confirm its properties. This resinous substance easily dissolves in alkali, and is precipitated again by acids. It gives a brownish blue colouration with ferric chloride and its alkaline solution lathers like soap. From these facts it may be inferred that the resinous substance contains the phenolic hydroxy group in its molecule.

I have obtained a small quantity of phthalic acid and a little

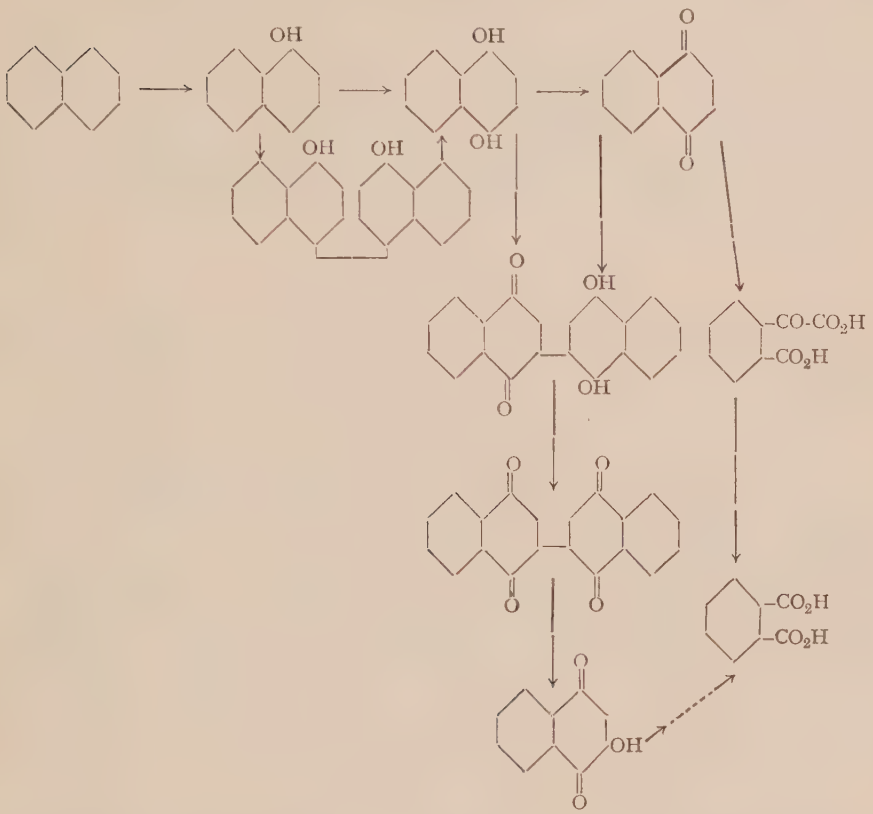
larger quantity of an insoluble black substance by the potash fusion of the resinous substance. A still larger quantity of phthalic acid was obtained by the oxidation with alkaline potassium permanganate. From these facts it can be expected that the resinous substance contains a naphthalene ring or a naphthoquinone ring. By distilling with zinc dust I have obtained a compound with yellowish blue fluorescence in the benzene solution. By converting it into the picric acid compound, it was found to consist of $\alpha\alpha$-binaphthyl and $\beta\beta$-binaphthyl. It can be thus presumed that condensation products of naphthalene exist in the resinous substance. From the facts that α-napnthol exists in the electrolytic solution and the brownish black substance possesses the phenolic property, there is little room to doubt that $\alpha\alpha$-binaphthol is produced as a step in the oxidation, as it is well known that $\alpha\alpha$-binaphthol is produced by the oxidation of α-naphthol with ferric chloride[11] and gives $\alpha\alpha$-binaphthyl by the zinc dust distillation.

Besides, C. Liebermann[12] observed that α-naphthoquinone is easily condensed into $\beta\beta$-binaphthyl-α-diquinhydrone, the latter being transformed into $\beta\beta$-binaphthyl by the zinc dust distillation and into phthalic acid by oxidation. Judging from the above behaviours, there is hardly room to doubt the formation of $\beta\beta$-binaphthyl-α-diquinhydrone as the intermediate product in this electrolytic oxidation. The smaller yield of α-naphthoquinone when acetic acid is used as the solvent, is perhaps due to the fact that α-naphthoquinone, produced by the electrolytic oxidation, is in a more suitable condition to change further to $\beta\beta$-binaphthyl-α-diquinhydrone.

On oxidizing the dark brown substance by the method of J. Stenhouse and C. Groves[13] I have obtained a small quantity of α-naphthoquinone, $\beta\beta$-binaphthyl-α-diquinone and a larger quantity of violet brown oxidation product.

I have now under investigation this dark brown resinous substance, and judging from the above results, I believe that the existence of $\alpha\alpha$-binaphthol and $\beta\beta$-binaphthyl-α-diquinhydrone in it is unquestionable.

From these results I venture to assume that the progress of reaction of the electrolytic oxidation of naphthalene may be represented by the following scheme :



During electrolysis in the sulphuric acid-acetone solution I always observed the accumulation of a red substance on the surface of the cathode solution. On exposing the cathode solution to the air after the electrolysis, the solution changes to red, and a red substance is precipitated in it. The cathode side of the porous cell, when it is used as the anode compartment, also changes to red. This red substance dissolves with a brownish yellow colour in a solution of sodium hydroxide, and it is again precipitated by dilute sulphuric acid. Extracted with benzene-alcohol solution, it dissolves with a red colour. On evaporating the solution on the water bath, it changes into a resinous substance. It gives a yellowish blue colouration with ferric chloride and a violet colouration with concentrated sulphuric acid. It is reduced by reducing agents. These qualitative results show that it has the quinone and phenolic properties. On a near occasion I hope to have a chance of studying the properties of this red substance and of clearing up its constitution.

Experimental Part

The refined naphthalene sold by druggists was further refined several times by the sublimation method. This substance melting at 80°, and its picrate melting at 149°, was used in the following experiments.

I. *Preliminary Experiment*

In order to ascertain what sort of substance is produced by the electrolytic oxidation of naphthalene, the following experiment were performed.

1. The anode liquid consisting of 50 c.c. sulphuric acid (20%), 150 c.c. of acetone and 5 grams of naphthalene was introduced into a beaker. A porous cell, successively washed with 1% alkali, water, 5% hydrochloric acid, and water, was placed in it as the cathode compartment. Sulphuric acid (20%) was taken as the cathode liquid, and a sheet of lead peroxide about 6.5 × 8.0 cm. served as the anode, while a sheet of lead served as the cathode. The beaker was cooled with water to keep the temperature of the bath always at about 20°. The electrolysis was continued for nearly 6 ampère hours with a current of 1.0 ampère.

After electrolysis the anode liquid was first extracted with ether and then with benzene. Each solvent was then evaporated, and the residues were mixed together and subjected to steam distillation. The distillation product that came out first was a white crystalline mass, then came out a yellow crystalline substance and at last red crystals in a very small quantity. The crystals were identified as α-naphthoquinone by the colour reactions with alcoholic phenylhydrazine[14] and with alcoholic aniline.[15] This was separated from the unchanged naphthalene by using light petroleum ether as solvent and was recrystallized several times from petroleum ether. It now melted at 125°. It was further characterized as oxime by heating with hydroxylamine hydrochloride by the method of H. Goldschmidt and H. Smidt.[16]

After cooling and separating the dark brown substance from the residue of the steam distillation, the liquid was extracted with a larger quantity of ether and was decolourized with animal charcoal. The ether was then evaporated off and the residue was sublimed, when a

small quantity of white crystalline needles was obtained. The melting point was found to be 128° and the substance was proved by the fluorescence reaction to be phthalic acid anhydride.

2. A sulphuric acid-acetic acid solution was tried under the following condition using the same apparatus as before:

Anode solution: 3 gr. naphthalene
150 c.c. glacial acetic acid
50 c.c. H_2SO_4 (20%)
Anode: Platinum (5.0 × 8.0 cm.)
Cathode solution: H_2SO_4 (20%)
Cathode: Spiral platinum
Current strength: 0.5 ampère
Current quantity: 7.0 ampère hours.

After separating the crystals from the distillate which was obtained in the same manner as in (I), a product was obtained by neutralizing the filtrate with crystallized sodium carbonate. The crystals and this new product were then mixed together. α-Naphthoquinone was detected in this mixture. Phthalic acid was detected in the residue of the steam distillation.

II. *Quantitative Investigation of the Oxidation Products*

Having now confirmed the fact that naphthalene can be oxidized into α-naphthoquinone and phthalic acid in the acid solution, I next attempted to determine the quantitative relations under various conditions. For this purpose the electrolysis was carried out in a closed apparatus (Fig. I) and a porous cell served as the anode compartment and the outer side of the cathode compartment was cooled or warmed to keep it at a definite temperature.

A. *Electrolytic Oxidation in Sulphuric acid-acetone Solution*

I. Influence of the anode material.

Anode solution: 3.8 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (20 c.c. of H_2SO_4 (sp. gr. 1.84) to 100 c.c. of water)
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)

Tempereture: 18–23°.

The *α*-naphthoquinone obtained was estimated by K. H. Meyer's method[17] and the phthalic acid was identified with the fluorescence reaction. In the Table the oxidizing efficiency is represented by the ratio of the oxidized naphthalene to the naphthalene taken.

Fig. 1.

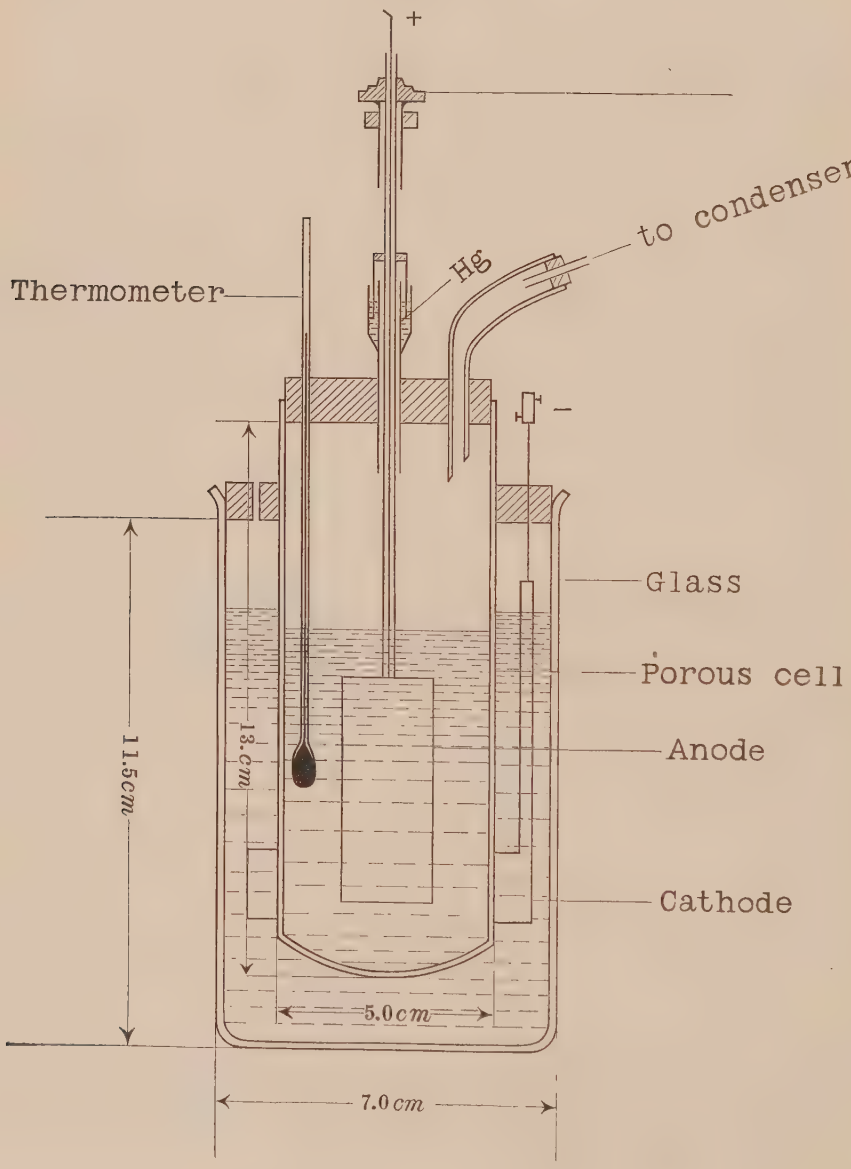


Table I.

Anode material	Anode surface area	Cathode material	Current strength	Voltage	Current quantity	Unchanged naphthalene	Currrnt yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Phthalic acid	Oxidizing efficiency
	sq. cm.		Amp.	Volt	amp. hrs.	gr.	%	gr.	gr.		%
Platinum	51.40	Spiral platinum	1.0	3.0—3.3	4.7	1.5716	3.25	0.1501	1.8397	+	58.64
Lead peroxide	55.40	Lead	1.1	3.1—3.3	4.73	1.5079	6.97	0.3240	1.9352	+	60.34
Nickel	40.99	Nickel	0.8	3.2—3.4	4.8	2.3727	0.95	0.0470	1.0712	—	37.56
Lead	55.40	Platinum	1.1	3.1—3.2	4.73	1.7575	2.42	0.1185	1.8256	+	53.75
Iron	45.55	Platinum	0.9	2.5—2.8	4.68	1.9612	2.08	0.0956	1.5833	—	48.39

II Influence of the concentration of sulphuric acid.

Anode solution: 3.8 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4

Anode: Lead peroxide

Cathode solution: H_2SO_4 (the same concentration as in the anode solution)

Cathode: Lead

Temperature: 18–23°

Current strength: 0.8 ampère

Current quantity: 4.73 ampère hours.

Table II.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
cm.	cm.	volt	gr.	%	gr.	gr.	%
10	100	2.8—2.9	1.7662	3.44	0.1660	1.6781	53.52
20	100	2.9—3.1	1.6473	5.44	0.2529	1.7205	56.65
30	100	3.0—3.2	1.7392	3.79	0.1660	1.6924	54.23
40	100	3.0—3.2	1.9805	2.04	0.0948	1.5147	47.88
50	100	3.2—3.4	1.0850	1.70	0.0790	1.4390	45.12

Anode solution: 2.0 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4

Anode: Platinum
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Spiral platinum
Temperature: 18–23°
Current strength: 1.0 ampère
Current quantity: 2.4 ampère hours.

Table III.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
cm.	cm.	volt	gr.	%	gr.	gr.	%
10	100	3.0—3.1	1.0192	1.82	0.0434	0.8253	49.04
20	100	3.0—3.3	0.8210	3.36	0.0790	0.9675	58.95
30	100	3.2—3.5	1.0170	2.85	0.0671	0.8002	49.15
40	100	3.4—3.7	1.2408	2.18	0.0513	0,5149	37.96
50	100	3.6—3.8	1.3476	1.68	0.0395	0.4381	32.62

III Influence of current density.
Anode solution: 3.8 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (20 c.c. of H_2SO_4 (sp. gr. 1.84) to 100 c.c. of water)
Anode: Lead peroxide
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Lead
Temperature: 18–23°.

Table IV.

Current strength	Voltage	Current quantity	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
amp.	volt	amp. hr.	gr.	%	gr.	gr.	%
0.6	2.7—2.9	4.698	1.8772	3.42	0.1580	1.6479	50.60
1.1	3.1—3.3	4.730	1.5079	6.97	0.3240	1.9352	66.34
1.6	3.8—4.1	4.800	1.4379	5.03	0.2371	1.9500	62.16
2.2	4.2—4.5	4.600	1.3877	2.62	0.1185	2.1047	63.48

Anode solution: 2.0 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
Anode: Platinum
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Spiral platinum
Current quantity: 2.4 ampère hours
Temperature: 18–23°.

Table V.

Current strength	Voltage	Unchanged naphthalene	Current yield of α-naphtho-quinone	α-naphtho-quinone	Dark brown substance	Oxidizing efficiency
amp.	volt	gr.	%	gr.	gr.	%
0.5	2.8—3.1	1.0270	1.98	0.0466	0.8728	48.65
1.0	3.0—3.3	0.8210	3.36	0.0790	0.9675	58.95
1.5	3.4—3.6	0.7136	4.18	0.0984	1.0137	64.32
2.0	3.5—3.8	0.6684	3.55	0.0834	1.0503	66.58
2.5	4.0—4.2	0.6392	3.10	0.0730	1.1026	68.04

IV Influence of electrolytic temperature.
Anode solution: 3.8 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
Anode: Lead peroxide
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Lead
Current strength: 1.1 ampère
Current quantity: 4.73 ampère hours.

Table VI.

Temperature	Voltage	Unchanged naphthalene	Current yield of α-naphtho-quinone	α-naphtho-quinone	Dark brown substance	Oxidizing efficiency
°c.	volt	gr.	%	gr.	gr.	%
18—23	3.1—3.3	1.5079	6.97	0.3240	1.9352	60.34
41—47	3.2—3.8	1.2821	5.62	0.2608	2.0406	66.26
55—67	3.6—4.2	1.2061	4.57	0.2122	2.1366	68.26

Anode solution: 2.0 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
Anode: Platinum
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Spiral platinum
Current strength: 1.0 ampère
Current quantity: 2.4 ampère hours.

Table VII.

Temperature	Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
°c.	volt.	gr.	%	gr.	gr.	%
18—23	3.0—3.3	0.8210	3.36	0.0790	0.9675	58.95
40—48	4.0—4.1	0.6852	4.48	0.1054	1.1325	65.74

V Influence of Current quantity.
Anode solution: 2.0 gr. naphthalene
100 c c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
Anode: Lead peroxide
Cathode solution: H_2SO_4 (The same concentration as in the anode solution)
Cathode: Lead
Current strength: 1.1 ampère
Temperature: 18-23°.

Table VIII.

Current quantity	Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	Material yield of α-naphthoquinone	α-naphthoquinone	α-naphthoquinone / current quantity	Dark brown substance	Oxidizing efficiency
amp. hr.	volt.	gr.	%	%	gr.	gr./amp. hr.	gr.	%
2.53	3.1—3.2	0.8056	3.71	4.61	0.0922	0.0364	0.9942	59.72
5.50	3.0—3.2	0.2784	2.28	6.17	0.1235	0.0224	1.2641	86.08
7.70	3.1—3.3	0.0940	1.94	7.34	0.1468	0.0190	1.4192	95.30

VI Influence of the oxygen carrier.

Anode solution: 3.8 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
1.0 gr. oxygen carrier

Anode: Lead peroxide

Cathode solution: H_2SO_4 (The same concentration as in the anode solution)

Cathode: Lead

Current strength: 1.1 ampère

Current quantity: 4.73 ampère hours

Temperature: 18–23°.

Table IX.

Oxygen carrier	Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
	volt.	gr.	%	gr.	gr.	%
Vanadic acid.....	2.9—3.1	0.9919	14.98	0.6955	1.9476	73.10
Chromealum	3.1—3.2	1.3136	9.36	0.4347	1.8924	65.43
Potassium chromate ...	3.0—3.2	1.0662	14.42	0.6694	1.9253	71.93
Manganese sulphate ...	3.0—3.1	1.2290	12.36	0.5737	1.8767	67.65
Potassium ferrocyanide.	3.0—3.3	1.2378	11.98	0.5563	1.8416	67.42
Cobalt sulphate	2.9—3.0	1.4376	8.17	0.3794	1.8464	62.16
Cerium Nitrate	3.2—3.3	0.8180	16.29	0.7560	2.0637	78.47
Mercuric sulphate	2.9—3.1	1.2740	10.51	0.4900	1.8717	66.47
Potassium chlorate ...	3.1—3.2	1.0382	14.80	0.6868	1.9005	72.66

Anode solution: 2.0 gr. naphthalene
100 c.c. acetone
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
1.0 gr. oxygen carrier

Anode: Platinum

Cathode solution: H_2SO_4 (The same concentration as in the anode solution)

Cathode: Spiral platinum

Current strength: 1.0 ampère

Current quantity: 2.4 ampère hours

Temperature: 40–50°.

Table X.

Oxygen carrier	Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
	volt.	gr.	%	gr.	gr.	%
Vanadic acid	3.3—3.4	0.4184	9.06	0.2135	1.1823	79.08
Potassium chromate ...	3.2—3.4	0.5128	6.01	0.1502	1.1636	74.36
Cerium sulphate.....	3.2—3.4	0.3652	9.80	0.2308	1.2614	81.74
Potassium chlorate ...	3.1—3.3	0.3972	8.38	0.1976	1.2112	80.14

B. *Electrolytic Oxidation in Sulphuric acid-acetic acid Solution.*

I Influence of concentration of sulphuric acid.

Anode solution: 2.0 gr. naphthalene
100 gr. glacial acetic acid
50 c.c. H_2SO_4

Anode: Platinum

Cathode solution: H_2SO_4 (The same concentration as in the anode solution)

Cathode: Spiral platinum

Current strength: 1.0 ampère

Current quantity: 2.4 ampère hours

Temperature: 50–60°.

Table XI.

Concentration of sulphuric acid		Voltage	Unchanged naphthalene	Current yield of α-naphthoquinone	α-naphthoquinone	Dark brown substance	Oxidizing efficiency
Sulphuric acid	Water						
c.c.	c.c.	volt.	gr.	%	gr.	gr.	%
10	100	3.3—3.4	1.2240	0.93	0.0221	0.6325	38.80
20	100	3.4—3.6	1.1637	1.57	0.0371	0.6687	41.81
30	100	3.2—3.4	1.0760	1.01	0.0240	0.7486	46.20
40	100	3.4—3.6	1.1900	0.43	0.0102	0.6180	40.50
50	100	3.5—3.6	1.3601	0.27	0.0065	0.4833	31.99

II Influence of the current density.

Anode solution: 2.0 gr. naphthalene
100 c.c. glacial acetic acid
50 c.c. H_2SO_4 (20 c.c. of H_2SO_4 (sp. gr. 1.84) to 100 c.c. of water)

Anode : Platinum
Cathode solution : H_2SO_4 (The same concentration as in the anode solution)
Cathode : Spiral platinum
Current quantity : 2.4 ampère hours.
Temperature : 50–60°.

Table XII.

Current strength	Voltage	Unchanged naphthalene	Current yield of α-naphtho-quinone	α-naphtho-quinone	Dark brown substance	Oxidizing efficiency
amp.	volt.	gr.	%	gr.	gr.	%
0.5	2.9—3.1	1.0810	0.80	0.0189	0.7268	45.95
1	3.2—3.4	1.0760	1.01	0.0240	0.7486	46.20
1.5	3.9—4.0	1.0452	1.13	0.0267	0.7476	47.74
2	3.8—3.9	1.0200	0.90	0.0212	0.7898	49.00

III Influence of the oxygen carrier.
Anode solution : 2.0 gr. naphthalene
100 c.c. glacial acetic acid
50 c.c. H_2SO_4 (The same concentration as in the previous experiment)
1.0 gr. oxygen carrier
Anode : Platinum
Cathode solution : H_2SO_4 (The same concentration as in the anode solution)
Cathode : Spiral platinum
Current strength : 1.0 ampère
Current quantity : 2.4 ampère hours
Temperature : 50–60°.

Table XIII.

Oxygen carrier	Voltage	Unchanged naphtha-lene	Current yield of α-naphtho-quinone	α-naphtho-quinone	Dark brown substance	Oxidizing efficiency
	volt.	gr.	%	gr.	gr.	%
Potassium chromate ...	3.3—3.4	0.6200	3.41	0.0804	1.2705	69.00
Cerium nitrate	3.4—3.5	0.5888	3.96	0.0934	1.1679	70.56
Potassium chlorate ...	3.3—3.4	0.6506	3.26	0.0770	1.0935	67.47

III. *The Oxidation Products of Naphthalene*

Ten grams of naphthalene were dissolved in a mixture of 200 c.c. acetone and 50 c.c. of sulphuric acid (20%). Lead peroxide (10×8 cm.) served as the anode and the electrolysis was continued for 26.4 ampère hours with a current of 1.6 ampères. The resultant product was treated in the same manner as in the preliminary experiment.

After separating the yellow crystals which were obtained by the steam distillation, the filtrate was extracted with ether. The ethereal extract was found to contain the *α*-naphthoquinone. The ether was cautiously distilled off, and the residue was combined with the yellow crystals. The unchanged naphthalene in the mixture was separated by means of light petroleum ether. The *α*-naphthoquinone, which was then recrystallized from the petroleum ether, was obtained in the form of beautiful yellow needles, melting at 125°. The yield was 0.5268 gram. The naphthalene was separated as picrate from the solution in light petroleum ether; the yield was 0.3519 gram.

α-Naphthoquinone isolated as above was analysed with the following results:

0.1935$^{gr.}$ substance gave 0.5353$^{gr.}$ CO_2 and 0.0641$^{gr.}$ H_2O.

	Found	Cal. ($C_{10}H_6O_2$)
Carbon	75.44%	75.93%
Hydrogen	3.70	3.83

After cooling the steam distillation residue and separating from it the dark brown substance, the liquid was extracted with a large quantity of ether. The ethereal extract was decolourized with animal charcoal and the ether was evaporated. A pale brown residue was thus obtained, which was separated by means of the solubility difference, into two components, soluble and insoluble in chloroform.

The part insoluble in chloroform was dissolved in dilute caustic soda solution and again precipitated with hydrochloric acid. After crystallizing from hot water and subjecting it to sublimation it was obtained in white needles. It melted at 128° and was proved, by the fluorescence reaction and by the volumetric analysis according to M. C. Boswell,[18] to be phthalic acid anhydride.

To neutralize 0.0324$^{gr.}$ substance there was required 4.3 c.c. N/10 NaOH Cal. 0.0318$^{gr.}$.

By evaporating chloroform from the soluble part a pale brown crystalline substance was obtained which was dissolved in hot water. To a portion of this water solution there were added a few drops of ferric chloride, when a brownish blue colouration was produced. Also a dark violet colouration was produced by adding a few drops of bleaching powder. I had thus an evidence of the presence of α-naphthol by the above colour reactions, but could not isolate it in a crystalline form.

On evaporating another portion of the water solution, a pale brown crystalline substance was isolated. It did not give a definite melting point, although, when dried at 115°, it melted at 144°, and was proved to be identical with phthalonic acid by a direct comparison with a specimen of that acid prepared by C. Graebe and F. Trümpy.[19]

IV. *The Dark Brown Oxidation Product*

I. Potash fusion.

Three grams of dark brown substance were mixed with 5 c.c. water and 3 grams of potassium hydroxide and heated for 3 hours at 200–250° in the oil-bath. After cooling the reaction product was extracted with a large quantity of ether and a considerable quantity of a black insoluble substance was obtained. On distilling off the ether, there remained some white crystals. The crystals were dissolved in caustic soda and reprecipitated with hydrochloric acid and after drying, purified by sublimation. The substance melted at 128° and was proved by the fluorescence reaction to be phthalic acid anhydride.

II. Oxidation with alkaline potassium permanganate.

Five grams of the dark brown substance were dissolved in a mixture of 7 grams of potassium hydroxide and 400 c.c. water and were warmed with water solution of 40 grams of potassium permanganate for some hours with occasional shaking until the latter was decolourized. When the oxidation was completed, the precipitated manganese dioxide was filtered off. The precipitate was boiled with a large quantity of water, filtered, and pressed. Both the alkaline filtrates were combined under stirring, and were slowly neutralized with concentrated sulphuric acid and evaporated to small volume. It was extracted with ether and, on distilling off ether, some pale brown crystals separated out. The existence of any volatile acid was disproved by the steam distillation,

which gave only a neutral product. On evaporating the distillation residue, a white crystalline substance was obtained which decomposed at 184° when recrystallized from hot water. The long white needles obtained by sublimation of this substance, melted at 128°. The substance was identified by the fluorescence reaction as phthalic acid anhydride.

Phthalic acid isolated as above was analysed with the following results :

0.2074$^{gr.}$ substance gave 0.4371$^{gr.}$ CO_2 and 0.0679$^{gr.}$ H_2O.

	Found	Cal. ($C_8H_6O_4$)
Carbon	57.47%	57.81%
Hydrogen	3.66	3.64

III. Zinc dust distillation.

Two grams of the dark brown substance were subjected to the zinc dust distillation according to Gattermann's method. The distillation product gave a deep yellow colour with a green fluorescence. It was extracted with a large quantity of benzene, when it gave a yellow substance with yellowish green fluorescence. It was carefully fractionated by means of the difference of solubility in alcohol.

The portion soluble in alcohol was recrystallized with alcohol and its benzene solution was added to the benzene solution of picric acid. When the picrate was purified by recrystallization from benzene, it formed reddish brown needles which melted at 145°. Judging from its melting point, it is presumably *αα*-binaphthyl picrate.[20]

The part insoluble in alcohol was dissolved in hot benzene, and added to the benzene solution of picric acid. The crystals formed were purified by recrystallization from benzene, when they came out as yellowish brown needles melting at 184–185°. After separating picric acid from the substance as ammonium picrate, the picric acid was estimated by E. Feder's method.[21] The substance was thus identified as *ββ*-binaphthyl picrate.

0.2213$^{gr.}$ substance required 6.2 c.c. of N/10 sodium thiosulphate.

	Found	Cal.
Picric acid	64.11%	64.33%

IV. Oxidation with nitric acid.

Three grams of dark brown substance were suspended in 200 c.c. of boiling acetic acid (30%), and 5 c.c. of nitric acid (sp. gr. 1.45) were slowly added with constant stirring. The mixture was heated for a few hours and then the brownish yellow liquid was filtered while hot. A flocky precipitate separated out on cooling. The precipitate and the mother liquor were extracted with ether and then the ether was carefully distilled off. The product thus obtained was distilled with steam and a very small amount of α-naphthoquinone was found in the distillation. On cooling and filtering the distillation residue, a pale brown crystalline mass was obtained, containing no nitrogen. It was purified by recrystallization from hot alcohol and was found to melt at about 215.5–217°, although the definite melting point was difficult to hit at. Judging by its melting point and its chemical behaviour, it is presumably $\beta\beta$-binaphthyl-α-diquinone prepared by F. Chattaway.[22] It was oxidized by alkaline potassium permanganate to phthalic acid. In addition to the above substance, I have also obtained a substance insoluble in acetic acid (30%) among the oxidation products with nitric acid. The investigation of this substance is not yet completed.

The author takes pleasure in heartily thanking Prof. M. Matsui for suggesting this research, and for his valuable guidance, and kindly interest throughout the work.

BIBLIOGRAPHY

1. Zs. Elektrochem., **8**, 673, (1902).
2. Zs. Elektrochem., **11**, 863, (1905).
3. F. Foerester: Elektrochemie wässeriger Lösungen, 735, (1915).
4. D. R. P., 1904, 152063.
5. D. R. P., 1906, 172654.
6. D. R. P., 1899, 103860.
7. C. Groves: J. Chem. Soc., **26**, 209, (1873); M. C. Boswell: J. Physical Chem. **11**, 128, 130, (1907).
8. Ber. **14**, 976, 1382, (1881).
9. Fr. Fichter and R. Stocker: Ber., **47**, 2003, (1914).
10. Fr. Fichter and E. Uhl: Helv. Chim. Acta., **3**, 22, (1920).
11. Dianin: J. d. russ. phys. chem. Ges., **6**, 183, (1874); Beilstein's Handb. d. org. Chem., 1896, 11, 1004.
12. Ber., **18**, 966, (1885).

13. Ann., **194**, 206, (1879).
14. J. Zinck and H. Bindewald: Ber., **17**, 3026, (1884).
15. R. Plimpton: J. Chem. Soc., **37**, 635, (1880).
16. Ber., **17**, 2064, (1884).
17. Ber., **42**, 1153, (1909).
18. J. Am. Chem. Soc., **29**, 235, (1907).
19. Ber., **31**, 369, (1898).
20. H. Walder: Ber., **15**, 2171, (1882).
21. J. Chem. Soc., **90**, ii, 809, (1906).
22. J. Chem. Soc., **67**, 661, (1895).

On the Solubility of Calcium Carbonate in Water in Equilibrium with a Gaseous Phase containing Carbon Dioxide

By

Yukichi Osaka

(Received May 14, 1921)

Carbonic acid has been well known as a very weak acid, but according to recent investigations it seems to be a much stronger acid than hitherto supposed. If such be the case, the chemical equilibrium of carbonic acid must necessarily be treated in somewhat different ways. From this point of view, the author calculated the solubility product of calcium carbonate, utilizing the existing data, and then derived a formula for the calculation of the solubility of calcium carbonate in water which is in equilibrium with a gaseous phase containing carbon dioxide of a given partial pressure. The results form the present article.

When carbon dioxide is dissolved in water a portion of it forms carbonic acid:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

and the carbonic acid thus formed dissociates electrolytically in two stages:

$$H_2CO_3 \rightleftarrows HCO_3' + H^{\bullet},$$

$$HCO_3' \rightleftarrows CO_3'' + H^{\bullet}.$$

If the concentrations of the molecules and ions be denoted by enclosing their formulas within brackets and the law of mass action be applicable to this case, the following equations are obtained:

$$K_0[CO_2] = [H_2CO_3], \tag{1}$$

$$K_1[H_2CO_3] = [H^\cdot] \times [HCO_3'], \tag{2}$$

$$K_2[HCO_3'] = [H^\cdot] \times [CO_3''], \tag{3}$$

where K_0, K_1 and K_2 are the respective equilibrium constants. The constant K_1 is the first dissociation constant of carbonic acid, but it is not what is generally taken as that constant. As the concentration of carbonic acid is generally taken the sum of carbonic acid and its anhydride and the so-called first dissociation constant K_1' is defined by the following equation:

$$K_1'([H_2CO_3] + [CO_2]) = [H^\cdot] \times [HCO_3']. \tag{4}$$

This is the apparent dissociation constant and the relation between the true dissociation constant and the apparent one is obtained from the equations (1), (2) and (4) as follows:

$$\frac{K_0 K_1}{1 + K_0} = K_1'. \tag{5}$$

As to the apparent dissociation constant, J. Walker and W. Cormack's determination,[1] 3.40×10^{-7} at 18°, has generally been used, but the following values given by J. Kendall[2] seem to be more accurate:

Temperature	0°	18°	25°
$K_1' \times 10^{-7}$	2·24	3·12	3·50

Walker and Cormack expressed the opinion that the carbon dioxide dissolved in water is in combination with it to an extent of at least more than fifty per cent. If that be the case, the true dissociation constant of the acid would be of an order of 10^{-7}, and carbonic acid be an acid very much weaker than acetic acid.

---

1 J. Chem. Soc., **77**, 5 (1900).

2 J. Amer. Chem. Soc., **38**, 1480 (1916).

From the behavior of aqueous carbonic acid on neutralisation, A. Thiel and R. Strohecker[1] came to the conclusion that in a 0·00812 molar solution at 4° only 0·67 per cent. of the total carbon dioxide dissolved in water is in combination with it. If the apparent dissociation degree may be negligible against unity, it is calculated to be 0·00608, and it follows that the true dissociation degree is 0·91. If the apparent dissociation constant at 4° be assumed to be 3×10^{-7}, the true constant will be 5×10^{-4}. Then Strohecker[2] reported that in a 0·008544 molar solution 0·56 per cent. of carbon dioxide is in combination with water, that the apparent dissociation constant at 4° as determined from the electrolytic conductivity is $2{\cdot}2 \times 10^{-7}$, and that the true dissociation constant is $4{\cdot}4 \times 10^{-4}$. Moreover L. Pusch[3] estimated by certain electrochemical methods the true dissociation constant of carbonic acid at 20° to be $7{\cdot}42 \times 10^{-4}$ in one case and $7{\cdot}01 \times 10^{-4}$ in the other.

As may be seen, the numerical values of the true dissociation constant found by Thiel and Strohecker on the one side and by Pusch on the other are not in good agreement, even if the difference in temperature be taken into consideration, but they show in common that the true dissociation constant is greater than 10^{-4} and that carbonic acid is a much stronger acid than acetic acid.

The apparent dissociation constant of carbonic acid at 4° as interpolared from the data given by Kendall is $2{\cdot}44 \times 10^{-7}$. If its true dissociation constant is assumed to be 4×10^{-4} at that temperature, from the equation (5) it follows:

$$K_0 = 0{\cdot}0006.$$

If K_0 be a magnitude of such an order, then it may be neglected against unity and the equation (5) may be simplified as follows:

$$K_0 K_1 = K_1'.$$

As to the second dissociation constant of carbonic acid, there are a number of data in the literature,[4] but the value, $K_2 = 4{\cdot}91 \times 10^{-11}$ at

1 Ber. D. chem. Ges., **47**, 945 (1914).

2 J. Chem. Soc. Abst., **110**, II, 522; from Z. Nahr Genus., **34**, 121 (1916).

3 Z. Elektrochem., **22**, 206 and 293 (1916).

4 G. Bodländer, Z. physik. Chem., **35**, 23 (1900); H. N. McCoy, Amer. Chem. J., **29**, 437 (1903); J. Stieglitz, Carnegie Inst. Publ., **107**, 233 (1908), &c.

25°, determined by C. A. Seyler and P. V. Lloyd,[1] seems to be most reliable.

Now, taking into consideration the fact that only a small portion of the carbon dioxide dissolved in water is in combination with it, and using the data, $K_1' = 3{\cdot}50 \times 10^{-7}$ and $K_2 = 4{\cdot}91 \times 10^{-11}$, the solubility product of calcium carbonate (calcite form) at 25° was calculated in the following way.

In a solution of calcium carbonate in water containing carbonic acid, it is electrolytically dissociated and also reacts with carbonic acid, namely:

$$CaCO_3 \rightleftarrows Ca^{\cdot\cdot} + CO_3''$$

$$CaCO_3 + H_2CO_3 \rightleftarrows Ca(HCO_3)_2 \rightleftarrows Ca^{\cdot\cdot} + 2HCO_3'.$$

Let K_3 denote the solubility product of calcium carbonate at 25°, then

$$[Ca^{\cdot\cdot}] \times [CO_3''] = K_3. \qquad (7)$$

From the equations (2), (3) and (7) the following relation is obtained:

$$\frac{[Ca^{\cdot\cdot}] \times [HCO_3']^2}{[H_2CO_3]} = \frac{K_1' K_3}{K_2}$$

and on combining the last equation with the equations (1) and (6) we have:

$$\frac{[Ca^{\cdot\cdot}] \times [HCO_3']^2}{[CO_2]} = \frac{K_0 K_1 K_3}{K_2} = \frac{K_1' K_3}{K_2} = K, \qquad (8)$$

where K is a new constant.

H. N. McCoy and H. J. Smith[2] determined the amounts of free carbonic acid and calcium bicarbonate in solutions in equilibrium with carbon dioxide of different partial pressures at 25°, and gave the results of six experiments as the typical representatives of the thirty-six experiments. Omitting the two cases in which the pressure of carbon dioxide was more than 15 atmospheres and the solubility of calcium carbonate became constant independent of the pressure of carbon dioxide, their results are quoted in the following table:

---

[1] J. Chem. Soc., **111**, 138 (1917).

[2] J. Amer. Chem. Soc., **33**, 468 (1911).

Table 1.

Approx. press. CO_2 in atmos.	Free carbonic acid.	Calcium bicarbonate	Dissoc. degree. γ
0·1	0·003522	0·004116	0·866
1·1	0·03728	0·009734	0·810
9·9	0·3329	0·02236	0·726
13·2	0·444	0·02495	0·713

Here the dissociation degrees were calculated under the assumption that they were equal to those of calcium acetate of the same concentrations, which were obtained from the electrolytic conductance data given in Kohlrausch and Holborn's *Leitvermögen.* These authors calculated, in the premises, that all the carbon dioxide dissolved is in combination with water, the solubility product of calcium carbonate, K_3, by the following equation:

$$\frac{\gamma[\mathrm{Ca(HCO_3)_2}]}{\sqrt[3]{[\mathrm{H_2CO_3}]}} = \sqrt[3]{\frac{K_1' K_3}{4K_2}} = K',$$

where $[\mathrm{Ca(HCO_3)_2}]$ denotes the total concentration of calcium bicarbonate and K' is a new constant. As the average of twenty-nine experiments they obtained $K'=0{\cdot}0234$ and then using the data, $K_1'=3{\cdot}04\times10^{-7}$ and $K_2=5{\cdot}5\times10^{-11}$, they obtained $K_3=9{\cdot}3\times10^{-9}$. If the other values for K_1' and K_2 as adopted by the present writer, namely $K_1'=3{\cdot}50\times10^{-7}$ and $K_2=4{\cdot}91\times10^{-11}$, be used, the same equation gives $K_3=5{\cdot}7\times10^{-9}$.

Now the solubility product of calcinm carbonate is calculated, contrary to McCoy and Smith's assumption, on the understanding that the so-called free carbonic acid in the solution all exists in the state of anhydride. The following table was thus obtained from the data given by McCoy and Smith by the use of equation (8):

Table 2.

$[CO_2]$	$[Ca^{\cdot\cdot}]+[Ca(HCO_3)_2]$	γ	$[Ca^{\cdot\cdot}]$	$[HCO_3']$	$K\times10^5$
0·003525	0·004116	0·866	0·003563	0·007126	5·140
0·03728	0·009734	0·810	0·007784	0·015768	5·260
0·3329	0·02236	0·728	0·01628	0·03256	5·184
0·444	0·02495	0·713	0·01779	0·03558	5·076
					5·163

In this table and also in the following pages the symbol $[Ca(HCO_3)_2]$, denotes the concentration of the undissociated calcium carbonate and not the total concentration of the bicarbonate, as was the case in the equation of McCoy and Smith. From the mean value of K the solubility product of calcium carbonate at 25° is calculated as follows:

$$K_3 = 5{\cdot}165 \times 10^{-5} \times \frac{K_2}{K_1'} = \frac{5{\cdot}165 \times 4{\cdot}91 \times 10^{-6}}{3{\cdot}50 \times 10^{-7}} = 7{\cdot}24 \times 10^{-9}.$$

Now the author proceeds to derive a formula for the calculation of the solubility of calcium carbonate in water in equilibrium with a gaseous phase containing carbon dioxide. In the calculation of the solubility product from the data of McCoy and Smith the presence of neutral calcium carbonate in the solution was not taken into consideration, but now more dilute solutions in contact with carbonic acid of much lower partial pressures are considered and it can not be neglected.

In a solution of calcium carbonate in water containing carbon dioxide there are the followiug equilibrium relations:

$$[Ca^{\cdot\cdot}] \times [CO_3''] = 7{\cdot}24 \times 10^{-9},$$

$$\frac{[H^{\cdot}] \times [HCO_3']}{[CO_2]} = 3{\cdot}50 \times 10^{-7},$$

$$[H^{\cdot}] \times [OH'] = 0{\cdot}82 \times 10^{-14},$$

and among the anions and cations the following relation must exist:

$$2[Ca^{\cdot\cdot}] + [H^{\cdot}] = [OH'] + [HCO_3'] + 2[CO_3'']. \qquad (9)$$

According to G. Just[1] the solution saturated with carbon dioxide of one atmosphere at 25° is 0·0338 molar, and as the solubility of carbon dioxide in water follows the Henry's law, if the partial pressure of carbon dioxide in the gaseous phase be denoted by P, expressed in atmospheres, the concentration of the free carbon dioxide in the solution is

$$[CO_2] = 0{\cdot}0338\ P.$$

Therefore

$$[H^{\cdot}] \times [HCO_3'] = 3{\cdot}50 \times 10^{-7} \times 0{\cdot}338P = 1{\cdot}183 \times 10^{-8}\ P,$$

[1] Z. physik. Chem., **37**, 342 (1901).

and

$$[H^{\cdot}] = \frac{1{\cdot}183 \times 10^{-8}\,P}{[HCO_3']},$$

$$[OH'] = \frac{0{\cdot}82 \times 10^{-14}}{1{\cdot}183 \times 10^{-8}\,P}[HCO_3'] = \frac{6{\cdot}93 \times 10^{-7}}{P}[HCO_3'].$$

It is evident that $[H^{\cdot}]$ increases and $[OH']$ decreases when P increases. From the experiments of McCoy and Smith it may be seen, that when P is of an order of 10, $[HCO_3']$ and $[Ca^{\cdot\cdot}]$ are both of an order of 10^{-2}, and in that case $[H^{\cdot}]$ may be neglected against $[Ca^{\cdot\cdot}]$ in the equation (9). Again, when $P=0{\cdot}0002$, $[OH']=3{\cdot}374\times 10^{-3}\,[HCO_3']$ and since $3{\cdot}74\times 10^{-3}$ may be neglected against unity without causing much error, $[OH']$ may also be neglected in the equation (9), provided P is not extremely small.

From the above equations we have

$$\frac{[HCO_3']^2}{[CO'']} = \frac{1{\cdot}183 \times 10^{-8} P}{4{\cdot}91 \times 10^{-11}} = 241\,P,$$

and since

$$[CO_3''] = \frac{7{\cdot}24 \times 10^{-9}}{[Ca^{\cdot\cdot}]},$$

we have

$$[Ca^{\cdot\cdot}] \times [HCO_3']^2 = 7{\cdot}24 \times 10^{-9} \times 2{\cdot}41 P = 1{\cdot}74 \times 10^{-6} P \qquad (10)$$

and

$$[Ca^{\cdot\cdot}] = \tfrac{1}{2}[HCO_3'] + \frac{7{\cdot}24 \times 10^{-9}}{[Ca^{\cdot\cdot}]} \qquad (11)$$

Now from the last two equations the values of $[Ca^{\cdot\cdot}]$ and $[HCO_3']$ may be obtained in the following way. For convenience the following symbols are used:

$$[Ca^{\cdot\cdot}]=x;\ [HCO_3']=y;\ 1{\cdot}74\times 10^{-6}P=a;\ 7{\cdot}24\times 10^{-9}=b;\ \tfrac{1}{2}=c;$$

then the equations (10) and (11) become

$$x^2 = cxy + b, \quad xy^2 = a.$$

On eliminating x between them we have

$$\frac{a^2}{y^4} = \frac{ac}{y} + b,$$

or

$$a^2 = acy^3 + by^4,$$

or

$$y^3(ac + by) = a^2.$$

Since $b/a = 4{\cdot}2 \times 10^{-3}/P$, $c = \frac{1}{2}$ and y is considerably smaller than P, by is much smaller than ac, it may be simplified in the following way:

It is transformed

$$y^3 ac\left(1 + \frac{b}{ac}y\right) = a^2,$$

or

$$y\sqrt[3]{ac} = \sqrt[3]{a^2}\left(1 + \frac{b}{ac}y\right)^{-\frac{1}{3}},$$

and then approximately

$$y\sqrt[3]{ac} = \sqrt[3]{a^2}\left(1 - \frac{1}{3}\frac{b}{ac}y\right),$$

or

$$y\left(\sqrt[3]{ac} + \frac{b}{3c\sqrt[3]{a}}\right) = \sqrt[3]{a^2}.$$

therefore

$$y = \frac{\sqrt[3]{a^2}}{\sqrt[3]{ac} + \frac{b}{3c\sqrt[3]{a}}},$$

or

$$y = \frac{3ac}{b + 3c\sqrt[3]{a^2c}},$$

and hence

$$x = \frac{b^2 + 6bc\sqrt[3]{a^2c} + 9ac^2\sqrt[3]{ac^2}}{9ac^2}.$$

Now on substituting the proper values for the symbols we have

$$[Ca^{\cdot\cdot}] = \frac{5{\cdot}24 \times 10^{-17} + 2{\cdot}49 \times 10^{-12}P^{2/3} + 2{\cdot}97 \times 10^{-8}P^{4/3}}{3{\cdot}91 \times 10^{-6}P}, \quad (12)$$

$$[HCO_3'] = \frac{2{\cdot}61 \times 10^{-6}P}{7{\cdot}24 \times 10^{-9} + 1{\cdot}72 \times 10^{-4}P^{2/3}}. \quad (13)$$

As the concentration of normal calcium carbonate is very small, it may be taken as completely dissociated, but as to the bicarbonate the dissociation must be considered as incomplete. As to the dissociation of the bicarbonate, it may be taken as the same as in the corresponding solutions of calcium acetate, as McCoy, Johnston[1] and others assumed. Let the degree of dissociation of the bicarbonate be denoted by γ, then the concentration of the undissociated part is

[1] J. Amer. Chem. Soc., **37**, 2001 (1915).

$$[Ca(HCO_3)_2] = \frac{1}{2}[HCO_3'] \frac{1-\gamma}{\gamma},$$

and the total concentration of the calcium in the solution is

$$C = [Ca^{\cdot\cdot}] + \frac{1-\gamma}{2\gamma}[HCO_3']. \qquad (14)$$

The values of γ were calculated from the data in Kohlrausch and Holborn's *Leitvermögen*, using for the migration velocities of the ions $\frac{1}{2}Ca^{\cdot\cdot}$ and HCO_3' the values 51·46 and 35·0 respectively. These data were all for 18°, but the values of γ thus calculated may be here used without bringing much error on the final result, especially when the partial pressure of carbon dioxide in the gaseous phase is low, as the author had intended. The values of γ calculated are given in Table 3.

Table 3.

$[C_2H_3O_2']$ or $[HCO_3']$	γ
0·0001890	0·945
0·0004665	0·933
0·000921	0·921
0·001808	0·904
0·004340	0·868
0·00831	0·831
0·01570	0·785

Any experiments at 25° which were worked with comparatively low partial pressures of carbon dioxide and might be utilized for the verification of the equations (12), (13) and (14) are not found in the literature. Thus the data at 16° published by Th. Schlösings[1] were taken and were compared with the calculated values for 25°. The result is represented in Table 4.

[1] C. R., **74**, 1555 (1872).

Table 4.

P	$[Ca^{\cdot\cdot}]\times 10^4$	$[HCO_3']\times 10^3$	γ	$[Ca(HCO_3)_2]\times 10^4$	C	
					Calc. (25°)	Obs. (16°)
0·000504	6·12	1·20	0·91	0·59	$6·7\times 10^{-4}$	$7·46\times 10^{-4}$
0·000808	7·15	1·41	0·91	0·70	7·9	8·50
0·00333	11·4	2·26	0·89	1·40	12·8	13·72
0·01387	18·2	3·62	0·87	2·70	20·9	22·31
0·02820	23·1	4·62	0·86	3·76	26·9	29·65
0·05008	28·0	5·59	0·85	4·93	32·9	36

As there is a difference of nine degrees in temperature, no good agreement can be expected, but it may be remarked that the calculated values are somewhat smaller than the observed and that this is qualitatively in concord with the fact that the solubility of calcium carbonate in water in contact with carbon dioxide of a given partial pressure decreases as the temperature rises.[1]

As may be seen from Table 4, when P is greater than 0·02829, exactly

$$[Ca^{\cdot\cdot}] = \tfrac{1}{2}[HCO_3']$$

and in that case the equation (12) and (13) may be simplified as follows:

$$[Ca^{\cdot\cdot}] = 7·6\times 10^{-3}P^{1/3},$$

$$[HCO_3'] = 1·52\times 10^{-2}P^{1/3}.$$

Summary

From the premises that carbon dioxide dissolved in water is combined with it only to a small extent and that carbonic acid is an acid much stronger than acetic acid, and using for the apparent first dissociation constant and the second dissociation constant of carbonic acid the values $3·50\times 10^{-7}$ and $4·91\times 10^{-11}$ respectively, the solubility product of calcium carbonate (calcite form) at 25° was calculated from the data given by McCoy and Smith to be $7·24\times 10^{-9}$.

1 Cf. Treadwell and Reuter, Z. anorg. Chem., **17**, 170 (1898).

Then the following formula was derived for the calculation of the solubility of calcium carbonate in water in contact with a gaseous phase of a given partial pressure of carbon dioxide:

$$C = [Ca^{\cdot\cdot}] + \frac{1-\gamma}{2\gamma}[HCO_3'],$$

where

$$[Ca^{\cdot\cdot}] = \frac{5{\cdot}24\times 10^{-17} + 2{\cdot}49\times 10^{-12}P^{2/3} + 2{\cdot}97\times 10^{-3}P^{4/3}}{3{\cdot}91\times 10^{-6}P},$$

$$[HCO_3'] = \frac{2{\cdot}61\times 10^{-6}P}{7{\cdot}24\times 10^{-9} + 1{\cdot}72\times 10^{-4}P^{2/3}}.$$

In this formula, C is the number of mols of calcium carbonate dissolved in one litre of water, P the partial pressure of carbon dioxide expressed in atmospheres, and γ the dissociation degree of calcium bicarbonate which is to be assumed to be the same as that of calcium acetate of the same concentration.

The Spectrum of the Luminosity of the Brush and the Glow Discharges of Electricity

By

Usaburo Yoshida and Hideki Hirata

(Received May 19, 1921)

In a previous paper[1] it was stated that the appearance of a positive brush at the anode of an influence machine was very similar to that of a tree; beginning from its start at the anode, it was divided into several branches which were also subdivided into many weak branchlets. Such a positive brush consisted of two parts, namely the intense luminosity near the anode and the weak luminosity as the continuation of the former. These two parts of the positive brush were different in their natures. The branches of the weak luminosity being a pilot of the other part of the intense luminosity, the arrival of the end of the latter at the cathode or at the negative brush caused, for the first time, a spark between the electrodes. In the case of the negative brush at the cathode of an influence machine, no such parts of the different natures as in the case of the positive brush were detected, and the mere arrival of the end of the negative brush at the anode or at the intense part of the anode brush gave rise to a spark between the electrodes.

When the positive and the negative brush discharge were made visible at each electrode respectively, and when a plenty number of negative ions was supplied uniformly to the anode, an entirely different phenomenon of discharge took place at the anode. The positive brush disappeared entirely and the surface of the anode which was just

---

1 Yoshida and Hirata, Mem. Coll. Sci. Kyoto, **4**, 89, (1919).

opposite to the cathode was now covered with a thin film of a pale violet positive glow as was stated in the previous paper.

Now in the present experiment, the luminosities in every part of the brush and the glow above stated in the air at ordinary pressure were spectroscopically examined separately. With a direct vision spectroscope the spectrum of the luminosity due to the brush and the glow discharges was photographed on panchromatic plates. The electric discharges of every kind above stated were made to take place on smooth surfaces of iron electrodes; and the spectrum lines of the spark between these iron electrodes were employed as the comparison spectrum for the determination of the wave lengths. As the luminosity of the brush and the glow discharges was very weak, the exposures of from four to eight hours were needed to take a photograph of a moderate intensity. From the photograph thus taken, it was observed that the spectrum of the brush and the glow was entirely the same for every kind of the brush and the glow discharges before mentioned, and that it was the band spectrum belonging to the second group of nitrogen. The head of every one of these bands being on longer wave side, they were diffused toward the opposite side. The wave lengths of the heads of these bands determined from the comparison spectrum of the iron spark are given in the following table.

The wave lengths in Å.U.

4667	4413	4267
4572	4353	4198
4487	4343	

The values of the wave lengths measured are in fair agreement with those given in Kayser's Handbuch der Spektroscopie for the heads of the bands belonging to the second group of nitrogen. Thus we may conclude that, in the case of the air at ordinary pressure, the luminosities of the positive glow, the negative brush, the stronger part of the positive brush and the weaker part of the positive brush are all the same and they are mostly due to the band spectrum belonging to the second group of nitrogen.

In conclusion the writers' thanks are due to Prof. Mizuno for the interest he has taken in the research.

The Secondary and the Tertiary Figures produced on Photographic Plates by Electric Discharges

By

Usaburo Yoshida and Shinsuke Tanaka

(Received May 19, 1921)

When one of the electrodes of an influence machine is placed on the sensitive film of a photographic plate and the other is connected to the metal plate under the photographic plate, and when a momentaneous brush discharge is made to occur on the photographic plate, a beautiful discharge figure will be impressed on the plate after developement. In the arrangement shown in Fig. 1, let P_1 P_2 be two photographic plates piled up by their glass sides, E be one of the electrode and M a smooth metallic plate separated from the sensitive film of the photographic plate P_2 by a small and thin insulating material whose thickness does not exceed ca. 0.5 mm. When by means of an influence machine a moderately high potential difference was applied momentaneously between the electrodes E and M, impressions of the brush discharges would be obtained on the photographic plate P_1 and P_2. Mikola[1] called the figure on the upper plate P_1 "the primary figure," and that on the lower plate P_2 "the secondary figure." Some examples of such figures are represented in Fig. 8 and Fig. 9. The figure b in Fig. 8 is the secondary figure corresponding to the primary negative

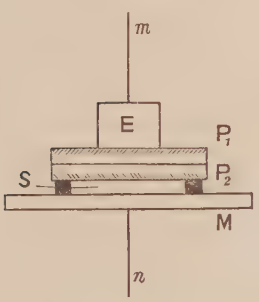


Fig. 1.

---

1 Mikola, Phys. Z.S., 18, 158, (1917).

brush a in Fig. 8. The secondary figure corresponding to the primary negative one consists of two parts: concentric rings which are at right angles to the branches of the primary negative brush, and the short branches which radiated outward from these rings. As these branches in the secondary figure are of the same nature as those in the positive brush discharge on a photographic plate, we may call it "the secondary positive figure" as Mikola[1] and Pedersen.[2] The secondary figure corresponding to the positive primary figure a in Fig. 9 is reproduced in b of the same figure. This secondary figure consists of a system of diffuse lines which are nearly at right angles to the branches of the corresponding primary positive figure. These diffuse lines in the secondary figure become more separated from each other with a thicker air space between the photographic plate P_2 and the metallic plate M. It was observed by the writers that these diffuse lines in the secondary figure, on some of the photographs taken with a sufficiently thick air space, had fine structures characteristic to the regular primary negative figure. Judging from this, the secondary figure corresponding to a primary positive one seems to be of a negative nature, and it may be called "the secondary negative figure" as Mikola and Pedersen.

If the arrangement is like that shown in Fig. 2, the primary figure will be impressed on the upper surface of the plate P_1, the secondary on the lower surface of the middle plate P_2 and the other "the tertiary figure" will be impressed on the upper surface of the plate P_3. When the electrode E on the photographic plates is positive, the primary figure is a positive one; the secondary and the tertiary are respectively a negative and a positive nature, and they are similar respectively to the negative and the positive secondary figures in the case of two photographic plates before mentioned. On the contrary, when the electrode E is made negative all of these three figures become to be of the opposite natures respectively. With four photographic plates P_1 P_2 P_3 P_4 and with two air spaces s_1 s_2 as shown in Fig. 3, four discharge figures may be obtained separately on each

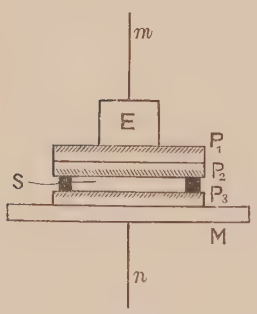


Fig. 2.

[1] Mikola, loc. cit.

[2] Pedersen, K. Danske Vidensk. Selskab, **1**, No. 11, 1, (1919).

plate. The figures on any two successive plates in this case are of the opposite natures as in the former cases. The figure impressed on the lower surface of the fourth plate P_4 being similar to that appeared on the lower surface of the second plate P_2, every one of these figures are respectively similar to the corresponding figures obtained in the cases of two and three photographic plates.

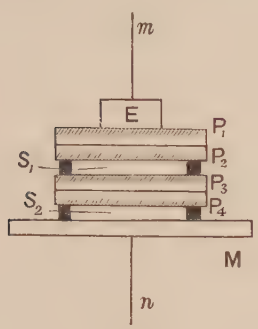


Fig. 3.

As regard to the secondary figure produced on the photographic plate P_2 in the arrangement shown in Fig. 1, explanations of its formation were given by Pedersen[1] and Toepler.[2] They considered that this secondary figures was the impression of the brush discharge in the thin air space between the photographic plate P_2 and the metal plate M beneath it. Actually the writers were able to detect that a weak glow appeared in this air space at the instant of the electric discharge; and the consideration given by Pedersen and Toepler seems to be a reasonable one. If we consider the primary cause of the formation of the secondary figure in the above manner, the fact that the nature of the branches of this figure on the photographic plate P_2 is of the same polarity as the metallic plate below it seems to be understood immediately.

It was already stated that the secondary figure both positive and negative consisted of a system of diffuse lines which were nearly at right angles to the branches of the corresponding primary figure. As regard to the explanation of this nature of the secondary figure, the writers' opinion is essentially the same as that given by Pedersen[3] and is described below.

In the sketch shown in Fig. 4, let E be the cathode, M the anode, P_1 P_2 two photographic plates and s be the air space between the anode M and the photographic plate P_2 as in the case of Fig. 1. When a sufficiently high potential difference is applied between E and M, brush discharges will take place on the upper side of the photographic plate P_1 and in the air space s. In the brush thus formed on the upper side of the plate P_1 a great number of negative ions will be

1 Pedersen, loc. cit.

2 Toepler, Phys. Z.S., **22**, 78, (1921).

3 Pedersen, loc. cit.

generated as conveniently indicated by the shaded part a_0 a_4 in the figure; and consequently by electric induction positive charges will be accumulated in the anode M as shown by the shaded part c_0 c_4. The vertical component of the intensity of the electric field in the air space s beneath the cathode will become very strong in this case, and the brush discharges will now occur across the air space s in this region. The irregular blackening of the photographic plate in the part of the secondary figure just beneath the electrode E may be due to these brush discharges. The free positive charge thus accumulated on the lower surfacc of the photographic plate P_2 by these brush discharges are conveniently shown by the shaded part b_0 b_1 in the figure. The shaded parts b_2 b_3 b_4 on the same photographic plate P_2 represent the distribution of the free charges on the diffuse lines in the secondary figure which are nearly perpendicular to the branches of the primary figure on the plate P_1. If the distribution of the electric charges at a certain stage of the formation of brush discharges be such as that shown in Fig. 4, then the vertical component of the electric field in the air space s will be weaker at the portion just in front of the place denoted by b_4 than at the place more remote such as represented by b_5. In this state of affair, when the range of the primary figure on P_1 is a little increased than a_4, the brush discharges across the air space s will occur at the place such as denoted by b_5, but not at the portion just in front of the place denoted by b_4. This state is present in all stages in the developement of the primary and the secondary figures. The fact that the secondary figure consists of a system of diffuse lines which are nearly perpendicular to the branches of the corresponding primary figure seems to be explanable in the above way. The distance between the two successive diffuse lines in the secondary figure increases with the thickness of the air space s and with the total thickness of the photographic plates P_1 P_2. This seems to be due to the fact that the variation of the vertical compo-

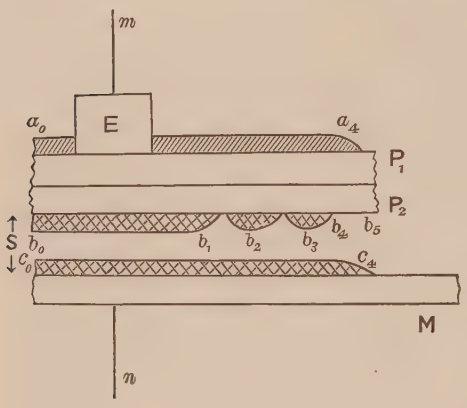


Fig. 4.

nent of the electric field in the neighbourhood of b_4 along the lower surface of P_2 become smaller as the thickness of the air space s and the total thickness of the photographic plate P_1 P_2 are increased. The next brush discharges across the air space s will now occur no more at the place denoted by b_5, but at the place more remote from b_4.

The electric charge accumulated on the lower surface of the photographic plate P_2 is due to the brush discharge across the air space s; and it is positive when the electrode M is anode. The horizontal component of the intensity of the electric field along the lower surface of the photographic plate P_2 will be very strong at the portion just in front of the place denoted by b_5; and consequently the positive brush will shoot out of b_4 and grow toward b_5 along the surface of the photographic plate P_2. The brush discharge across the air space s at b_5 will, if occur, be previous to the arrival of the terminals of the positive brushes above stated to b_5; and these latter positive brushes will be prevented from arriving at the place denoted by b_5 on account of the accumulation of positive ions on b_5 by the former brush discharge. This seems to be the reason that all brushes in the secondary positive figure, which are generated from a diffuse line perpendicular to the branches of the corresponding primary negative figure, do not reach the next diffuse paralled line in the same secondary figure. For the explanation of the secondary negative figure we are only to reverse the signs of all the charges.

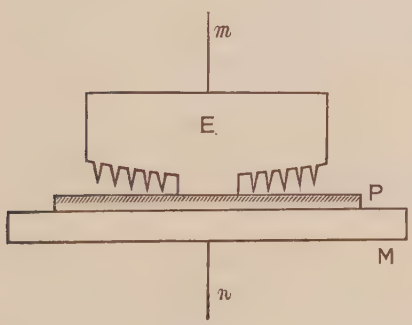


Fig. 5.

The main features of the secondary figures may be imitated by using the arrangement shown in the sketch in Fig. 5. Here M is a plate electrode, P a photographic plate and E is the other electrode placed on the film side of the photographic plate P. The electrode E has many circular and concentric sharp edges on its lower surface. These circular edges are so made that the small distance between the photographic plate P and any one of these edges increases regularly by a small amount as we recede from the center of the electrode. The brush discharges take place in this case between these circular edges and the photographic plate and also from the central part

of the electrode E along the film side of the photographic plate. The photographs obtained under such a condition are represented in Fig. 10. The figure a in Fig. 10 is the photograph obtained when the electrode E is anode, and the figure b is that obtained when E is cathode. These figures are very similar to the secondary positive and negative figures respectively in their main features.

It is already stated that, when the three photographic plates as shown in Fig. 2 are employed, the natures of the figures on these successive photographic plates are of the opposite polarity alternately. Thus, for example, when the primary figure is positive the secondary is negative and the tertiary figure is positive. The primary cause of the formation of the secondary and the tertiary figures in this case will be the brush discharge across the air space s in Fig. 2; and the positive and the negative ions generated by this brush discharge will be attracted towards the photographic plates P_2 P_3. The ions thus accumulated on the lower surface of P_2 will be negative, and those accumulated on the upper surface of P_3 will be positive. Consequently the figure on the upper surface of P_3 will be positive, and that impressed on the lower surface of P_2 will be negative contrary to the primary positive figure impressed on the upper surface of the plate P_1. For the explanation of the secondary positive and the tertiary negative figures we are only to reverse the signs of the charges.

It is also stated before that, the same phenomenon as described above has happened in the case of the four photographic plates arranged as shown in Fig. 3. A quite similar explanation as that given for the case of three photographic plates seems to be true also in this case.

The nature of the tertiary and the quartan figure is essentially the same as that of the secondary one; and it seems to be explained similarly as in the case of the secondary figure obtained in the arrangement shown in Fig. 1.

In the case of the secondary positive figure obtained under the condition represented by Fig. 1, the direction of the growth of the short positive brushes which originated from the diffuse lines perpendicular to the branches of the corresponding primary negative figure are toward outside as was stated before. But this is not always the case when some insulating material such as glass plate or paraffin paper &c. are introduced between the photographic plate P_2 and the metal plate electrode M as shown in Fig. 6. In this figure, E is one

of the electrodes, P_2 the photographic plate whose thickness was about 1 m.m. in the present case, and P_3 is the insulating material; between P_2 and P_3 there is an air space s whose thickness was 0.12 mm. in the present case. Under such experimental conditions, the direction of the growth of the short positive brushes in the secondary positive figure impressed on the lower surface of the photographic plate P_2 is different according to the thickness of the insulating plate P_3. When the thickness of this insulating plate is about 0.1 mm. the direction of the growth of these short positive brushes is toward outside; but when it is about 1 mm. these positive brushes grow in the opposite direction. This nature of the positive brushes in the secondary figure is represented by Fig. 11. In the case of the figure a in Fig. 11 the thickness of the insulating plate P was 0.1 mm., and the direction of the short positive brushes is toward outside. The thickness of the insulating plate in the case of the figure b in Fig. 11 was 0.75 mm., and the direction of the growth of the short positive brushes is reversed in this case. With a proper intermediate thickness of the plate P_3, the writers were able to observe that any such positive brush did not appear in the secondary positive figure as shown in Fig. 12, the thickness of the insulating plate P_3 being 0.25 mm. in this case.

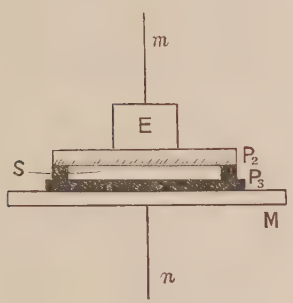


Fig. 6.

In Fig. 7, E is the cathode, M the anode, P_2 the photographic plate and P_3 is the insulating plate as in Fig. 6. The shaded parts in this figure represent the distribution of positive and negative electric charges in a certain stage of the developement of the brush discharges along the surface of the insulating plate P_3 and the photographic plate P_2. The negative charges set free in the primary negative brushes on the upper surface of the plate P_2 are represented by the shaded part a_1 a_4; and the positive charges in the anode M are shown

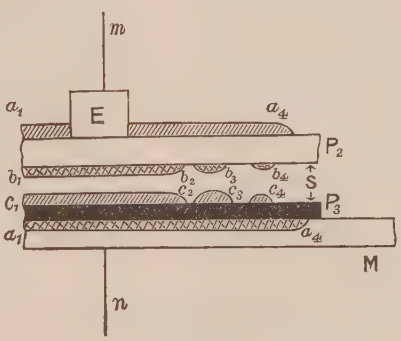


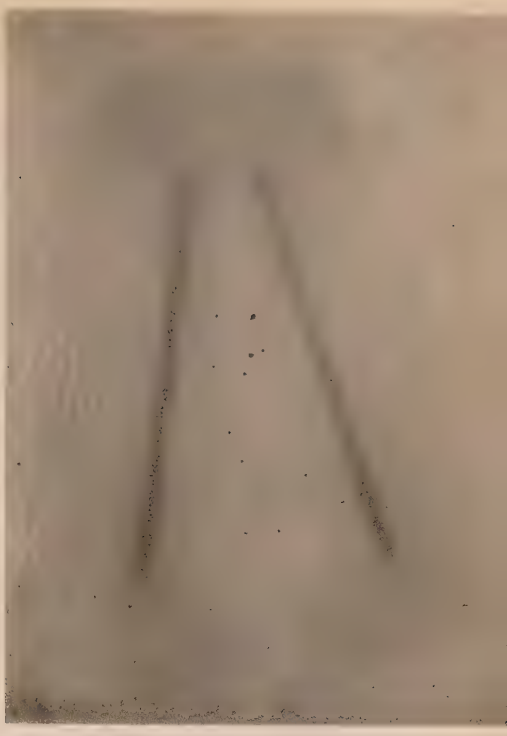
Fig. 7.

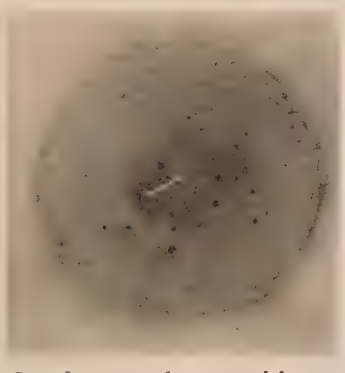
by d_1 d_4. Positive and negative charges accumulated respectively on the lower surface of P_2 and on the upper surface of P_3 are caused by the brush discharges across the air space s between the plates P_2 P_3, and they are roughly represented by the shaded parts b_1 b_2 b_3 b_4 and c_1 c_2 c_3 c_4 as in the case of Fig. 4. The charges in the shaded parts b_1 b_2 b_3 b_4 are evidently positive and those in c_1 c_2 c_3 c_4 are negative. The positive electric charge in the shaded part b_4 will be attracted by the negative charges in a_1 a_4 and in c_1 c_2 c_3 c_4 and will be repelled by the positive charges in d_1 d_4 and b_1 b_2 b_3. The intensity of the repulsive force due to the positive charge in the anode M is different according to the thickness of the insulating plate P_3, and is greater with a thinner plate than with a thicker one. Considering this, it seems very provable that, when the thickness of the insulating plate P_3 is sufficiently large, the horizontal component of the electric field along the lower surface of the photographic plate P_2 at b_4 acts toward inside; and that, on the contrary, it acts toward outside when the plate P is very thin. As we have no exact information as to the distribution of the electric charges in this case, the above consideration is not of course conclusive. But the behavior of the secondary positive figure on the lower surface of the plate P_2 i.e. that the direction of the growth of their short branches is different according to the thickness of the insulating plate P_3 seems very probably to be explained in the above mode.

The arrangement shown in Fig. 2 is essentially the same as that represented in Fig. 6. The only difference is that the two photographic plates are employed in this case instead of one. The part played by the insulating plate in the case of Fig. 6 is now occupied by the photographic plate P_3 whose thickness was about 1 mm. in the present experiment. The secondary positive figure impressed on the lower surface of the photographic plate P_2 consists of a system of diffuse lines perpendicular to the branches of the corresponding primary negative figure on P_1 and short positive brushes originated from these diffuse lines and terminated toward the inside of the figure. As regard to the direction of the growth of these short positive brushes, the same explanation as before seems to hold true also in this case.

In conclusion the writers' hearty thanks are due to Prof. Mizuno for his interest in the research.

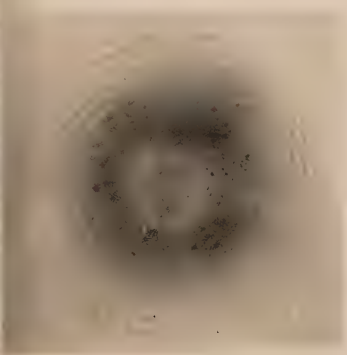
a, primary positive. Fig. 9. *b*, secondary negative.

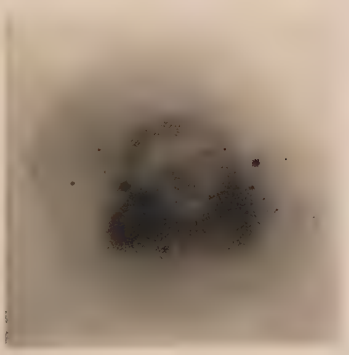




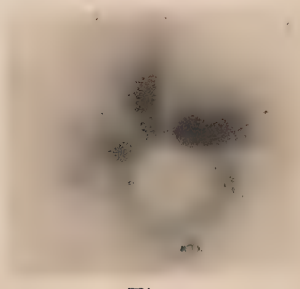
a, primary negative. Fig. 8. *b*, secondary positive.

Fig. 10.





a. Fig. 11. *b*.



Influences of the Presence of Gases or Vapours upon the Intensities of the Lines of the Secondary Spectrum of Hydrogen

By

Masamichi Kimura and Mitsuharu Fukuda

(Received May 28, 1921)

The object of the present experiment is to study the influence of gases and vapours upon the lines of the hydrogen spectrum. Of the lines of the Balmer series of hydrogen, Liveing and Dewar[1] have found that in the mixture of the more volatile gases of the atmosphere, namely, neon and helium, with hydrogen, the Balmer series could be traced as far as the ninth member. Merton and Nicholson[2] also have obtained similar results in hydrogen containing helium at high pressures. It was also known that the relative intensity of the secondary spectrum of hydrogen is greatly reduced by the presence of oxygen in vacuum tube containing hydrogen.

As to the secondary spectrum, interesting results were recently obtained by Merton.[3] He found that when hydrogen at a partial pressure of less than a millimeter was present in helium tube filled at a pressure of about 40 mm. the spectrum was remarkably different from that of the pure hydrogen. In the red and yellow regions it was found that a larger number of lines enhanced greatly in the tube containing helium, while other lines became weak or disappeared; in

1 Proc. Roy. Soc. **67**, 467 (1900).
2 Proc. Roy. Soc. **96**, 112 (1919).
3 Proc. Roy. Soc. **96**, 382 (1920).

the more refrangible part of the spectrum there was a little difference. He examined also the changes in the relative intensities of lines due to a variation of the pressure in a hydrogen tube, and showed that the Fulcher bands become relatively brighter at low pressures, and that at the same time there is a marked enhancement of the lines in the region about from $\lambda 5700$ to $\lambda 5000$. In the more refrangible part of the spectrum there was no conspicuous change in the relative intensities of lines except that the continuous background was reduced as the pressure was lowered.

Our experiments have shown that in a pure hydrogen, lines of Fulcher group I[1] are relatively intense at low pressures, while those belonging to the group II weak. At high pressures the latter lines and those lines, which were greatly enhanced in the hydrogen-helium tube of Merton, increased their intensities. These results led us to the study of the influence of different gases and vapours upon the secondary spectrum of hydrogen.

Hydrogen tubes used in the present experiment were of the form of an ordinary Geissler tube having side tubes. In the case of hydrogen and hydrogen-mercury tubes, aluminium wire electrodes were used, but for the hydrogen-chlorine, hydrogen-bromine and hydrogen-sulphur tubes their salts were employed as the electrodes. The hydrogen was prepared by heating a pieces of metallic sodium which has property to absorb an amount of pure hydrogen and evolves it when heated. In one of the side tubes, a small clean piece of metallic sodium free from oil was placed, and the whole tube was thoroughly evacuated by means of a Gäde-pump. During the evacuation the sodium was gently heated by a small flame to give off the gas, and the tube was washed with hydrogen, and then sealed at a high vacuum. When the side tube containing sodium was heated by a fine jet of a gas flame, occulded hydrogen makes its appearance. With the tube of such a form, it was difficult to determine directly the pressure of hydrogen in the tube, but its rough estimate was done by comparing the striae in the glow discharge with those of another tube of equal dimensions connected to a manometer. The pressure of hydrogen in the discharge tube was increased by heating the sodium and the corresponding variation of the intensities of lines in the secondary spectrum was studied by a two-prism spectrograph having a photographic objective of 50 cm. focus.

[1] Astrophy. J. **37**, 60 (1913).

In a hydrogen-mercury tube, a small quantity of pure mercury was put in a part of the discharge tube remote from the sodium, and the partial pressure of the mercury was varied by heating it.

In a hydrogen-chlorine tube, a second side tube containing a small amount of cupric chloride was employed and chlorine was driven out by heating it with a small flame. But the result being not satisfactory, it was decided to use tubes having salt electrodes. Even with this form of tubes it was not easy to regulate the vapour pressures of both hydrogen and chlorine, and a number of photographic plates used were found to be quite useless for the purpose. The same difficulty was also met with in preparing hydrogen-bromine tubes, so that silver bromide was used as the electrodes. These tubes were excited by an induction coil giving 30 cm. spark.

Influence of the Pressure of Hydrogen upon the Intensity Distribution of the Lines of Secondary Spectrum

The hydrogen tube described above was excited by an uncondensed discharge from 30 cm. induction coil and the light emitted from the side of the capillary was photographed with the above spectrograph on an Ilford panchromatic plate. During the exposure to the spectrograph striae in a wider portion of the tube was carefully watched, and if a change was detected in its appearence, a small drop of sodium was slowly heated to give an amount of the hydrogen gas so as to keep its pressure nearly constant. An exposure of 15 minutes was sufficient to secure a good plate for the tube containing hydrogen at a very low pressure. Reproduction of the spectrograms thus obtained are shown in Figs. 1 and 2 PL. I., the former representing a slightly underexposed one for faint lines, while the latter fully exposed.

Now, Fulcher has studied the spectrum of low potential discharge in hydrogen, and found that the spectrum for the low voltages is very simple when compared with an ordinary Geissler tube spectrum, the strongest lines being arranged with some regularity. For the sake of comparison, a reproduction of his spectrograms is given in Fig. 5 [taken from Fig. 3, PL. II. Astrophy. J. **37**, 60 (1913)]. An remarkable similarity will be observed between our secondary spectrum of hydrogen emitted from the discharge tube containing the gas at very low pressure and Fulcher's one of hydrogen excited by cathode rays having slow velocities. This is seen at once when Fig. 1 and

Fig. 5 were compared. Fig. 5a represents the hydrogen spectrum excited by the cathode rays having the velocity corresponding to the potential difference of 50 volts, Fig. 5b that of the Geissler tube and Fig. 5c that excited by the cathode rays of 35 to 45 volts. The dispersion and magnification of these two spectra are not equal, but the corresponding lines are indicated, and their similarity is soon recognized.

Fulcher has also shown that there is certain differences in the secondary spectrum for high and low potential discharges. He classified the lines into two groups, the first containing all the lines which are equally intense in high and low potential discharge spectra, and the second containing those which are relatively much weaker in the low potential one. He further remarked that to the first group all the lines between λ5700 and λ6300 which, according to Dufour, do not show a Zeeman effect, while to the second group belong all the lines with the effect.

Such a difference in the lines of the secondary spectrum of hydrogen was seen in the spectra emitted by hydrogen at high and low pressures. Now the authors found that when the hydrogen pressure was increased, certain changes were brought out in the intensity distribution of the lines. Fig. 3 shows an enlarged reproduction of the spectrum emitted by hydrogen at a relatively high pressure, the discharge presenting a number of luminous threads in the capillary part, and Fig. 4 the same spectrum slightly underexposed. In these reproductions lines are too crowded to point out clearly the change produced by the raise of the hydrogen pressure, so that highly magnified spectrograms of high and low pressure hydrogens are given in Fig. 6, in which A representing spectrum of a high vacuum discharge, and B that of a low vacuum one.

A first glance at these spectrograms shows that the lines lying on the long wave length side of λ6240 and those in the region between λ5690 and Hβ get fainter as the hydrogen pressure was raised. In the region between these, changes in intensities of lines are observed at various parts of the spectrum. Remarkable changes will be noticed at a set of lines lying between λ6183 and λ6162, λ6098 and λ6068, λ5944 and λ5968, and λ5896 and λ5878.

A closer examination of these two spectra A and B showed that a certain number of lines were reduced in intensity, while other behaved in an opposite way as the hydrogen pressure was increased. Here we

met with a difficulty to determine the correct exposures to be given to the low and high pressure tubes. But for the present purpose it is sufficient to make comparison of the relative intensities and this was done in the following way: a number of different exposures were given to the both, and relative intensities of lines in the spectrum of low presssre hydrogen were compared with these in the spectrum of the high pressure one.

Table I.

Lines weakened when hydrogen pressure was raised.

	Wave lengths	Fulcher Group	Low	High
S_3	6428	I	3	3
	6400	I	4	3
	6372	—	—	—
S_3	6327	I	9	9
	6300	I	6	5
S_7	6285	I	3	2
	6272	I	1	1
S_1	6238	I	5	5
S_3	6225*	I	11	11
S_7	6183	I	5	4
	6170	—	—	—
S_3	6122*	I	12	12
S_4	6098	—	—	—
S_5	6096*	I	6	6
S_7	6080*	I	7	8
S_3	*6018**	I	16	14
S_4	*5994**	I	2	$2\frac{1}{2}$
S_7	*5976**	I	10	10
	5950	I	5	5
	5895	—	—	—
	5823*	I	5	6
S_3	5713	II	1	4
	5656	I	3	5
	5612	II	$\frac{1}{2}$	5
	5538	I	10	8

Table II.

Lines enhanced when hydrogen pressure was raised.

Wave lengths	Fulcher Group	Low	High	H.	H-He.
6174	II	0	4	—	w
6162	—	—	—	6	8
6089	—	—	—	0	4
6070	I	4	6	—	w
6068	I	4	6	—	w
6032	I	7	12	10	12
6028	I	7	12	—	w
5989	I	2	3	—	w
5983	II	$\frac{1}{2}$	6	8	10
5968	—	—	—	—	w
5939	II	3	9	8	10
5931	—	—	—	8	10
5917	II	1	5	7	8
5885	—	—	—	—	w
5849	—	—	—	4	8
5847	—	—	—	0	5
5836	I	7	10	—	w
5831	—	—	—	2	7
5813	—	—	—	6	10
5804	II	$\frac{1}{2}$	4	2	4
5801	—	2	4	2	4
5794	—	—	—	3	8
5791	—	—	—	4	8
5779	—	—	—	3	6
5766	—	—	—	—	—
5759	II	2	7	—	w
5756	I	3	5	—	3
5703	II	1	8	2	7

After examination of these plates it was ascertained that the lines given in Table I suffered reduction in intensity when the hydrogen pressure was raised. In the table, the first column gives the lines whose wave-length are taken from Watson's measurement, and I in the second column denotes the lines of the group I classified by Fulcher and II those of the group II. The numbers in the third column under "low" represent intensities of lines in the low potential discharge spectrum obtained by Fulcher, while these in the fourth column under "high" the intensities in his high potential discharge spectrum.

Thus it will be observed that all the lines with exception of a few ones, belong to the group I of Fulcher, which are almost equally intense both in the high and low potential discharge spectra. Now, Merton[1] studied the effect of an addition of helium at a high pressure to hydrogen upon the change in intensity distribution of the lines of its secondary spectrum and showed that a set of lines get fainter, while others enhanced or remained unchanged. We see that lines in the above table were, by the addition of helium at a high pressure, also reduced, the only exception being a few lines printed in italic, which, according to Merton, remained unaffected by such a pressure of helium. The lines marked with * show, after Dufour, no Zeeman effect, and those with mark S_1, S_3, S_4, S_5 or S_7 indicate the member of lines belonging to the corresponding band line series.

Beside this change, lines enhanced by the increasing pressure of hydrogen are given in Table II, where lines denoted by I or II in the second column indicate those belonging to the group I or II respectively, the numbers under the headings "low" and "high" representing the same thing as those in the Table I. In the last two columns the intensities of the lines determined by Merton in the spectra of hydrogen and that mixed with helium at 40 mm. pressure were given, w in the last column showing the lines whose intensities were reduced by the addition of the helium.

Thus it will be seen that lines enhanced by raising the pressure of hydrogen are those whose intensities are stronger in the high potential spectrum than those in the low potential one. In the case of addition of helium at a high pressure this class of lines was not affected in the same way.

---

[1] Proc. Roy. Soc. **96**, 382 (1920).

Generally an addition of helium at a high pressure to hydrogen brought out a great change in the intensities of lines. According to Merton, the most conspicuous changes occurred in the less refrangible regions. In the green and the more refrangible parts of the spectrum all the lines were greatly reduced in intensity in the spectrum of hydrogen mixed with helium. But in the red and yellow regions a large number of lines were greatly enhanced in the spectrum of the mixture, while another set of lines became very weak. He supposed that a separation of the lines in the secondary spectrum of hydrogen into physically related groups has been caused by the addition of a large quantity of helium.

Our result has also shown that the raise in the pressure of hydrogen weakens the lines in the green and in the more refrangible parts of the spectrum. Lines in the yellow and the red suffered selective changes in intensities, while those lying in the less refrangible side of $\lambda 6200$ were generally reduced. Lines selectively reduced were also influenced in the same way by the addition of the helium, but all the lines strengthened did not show the same behaviour toward the addition of the helium, some being reduced in intensities by the helium, while the other enhanced. It is difficult to decide from this experiment whether this opposite behaviour of a few lines is due to the selective action of the atoms of helium and hydrogen, or simply due to the difference in pressure to which hydrogen molecules are subjected. But at any rate the grouping of the lines in the secondary spectrum into physically related classes might be caused by simply raising the pressure of hydrogen.

Water Vapour tube

The distribution of intensities in the lines of the secondary spectrum emitted by a tube containing water vapour at a very small pressure was almost equal to that of hydrogen at a low pressure.

The lines of the Balmer series was generally stronger in water vapour. Increasing the pressure of the vapour, the spectrum suffered the corresponding changes in the intensities of lines, just as in the case of the tube containing hydrogen only. A number of lines characteristic to the mixture of hydrogen and helium were also observed in the spectrum emitted from a tube containing a sufficient amount of the water vapour.

Hydrogen-Mercury Tube

Lewis[1] found that the addition of small quantities of mercury vapour to pure hydrogen materially reduced the intensities of both the lines of the secondary spectrum and of the Balmer series. He also mentioned that the relative intensities of spectra of hydrogen and mercury seemed to be proportional to their relative densities below 6 mm. hydrogen pressure. But his result seemed not to deal with the individual lines of the secondary spectrum. In the present experiment an influence of mercury vapour upon the individual lines of the secondary spectrum was studied, and it was shown that the secondary spectrum get much simpler as the pressure of mercury was raised.

The structure of the secondary spectrum emitted by hydrogen at a pressure of a few centimeters was not sensibly affected by the presence of mercury vapour at small pressures. But when a drop of mercury in one end of the tube was heated, the colour characteristic to mercury began to appear in the capillary, while the pink light due to hydrogen became fainter. Fig. 7 gives the spectrum taken in such a state, and for the sake of comparison hydrogen spectra at low and high pressures are again reproduced in Fig. 10 and Fig. 11.

It shows that all the lines given in Table I were also reduced by the increasing pressure of mercury vapour, while lines in table II behaved in the opposite way. Further increasing the pressure of mercury all the lines lying between λ6239 and Hα disappeared entirely, while lines on the short wave length side of the yellow mercury lines became very faint. The lines outside these regions suffered also a general reduction in intensities, but a number of intense lines were still seen in the region from λ6200 to λ5780. This is seen from the spectrogram given in Fig. 8. When the mercury pressure was further raised the lines again lost their brightness, and then all the lines except λ6032, 6018, 5976, and a few lines lying between λ5896 and λ5870 disappeared.

In the list of lines given by Merton, strong lines emitted from the mixture of hydrogen and helium at a high pressure are *6032(12) *6018(10) 5982(10) *5975(10) 5938(10) 5371(10) and 5812(10), but the lines except those with the mark * were killed more easily than the other by the mercury vapour at high pressures. These lines

[1] Astrophy, J. **10**, 137 (1899).

too died away as the pressure was further raised, leaving the lines of mercury only.

The change produced in the spectrum of hydrogen described above seems to consist partly of a general reduction of intensity, and partly of a somewhat selective one. This selective action of mercury vapour has some common nature with that of helium at a high pressure toward hydrogen, and it seems to be very important to see whether the action of mercury is the same as that of helium. In our experiment it was, however, very difficult to keep the pressure of mercury constant during the exposure to the spectrograph, and a similar spectrum as obtained by Merton in the mixture of hydrogen and helium could not be obtained.

Hydrogen-Bromine Tube

Tubes employed were of the form of an ordinary Geissler tube having silver-bromide electrodes and a side tube containing a piece of sodium. With the tube of this construction it was almost impossible to regulate the pressure of both hydrogen and bromine, so that the effect of bromine vapour of a few millimeters pressure upon the secondary spectrum emitted by hydrogen was only studied. Generally presence of the bromine vapour of such pressures reduced the intensity of the secondary spectrum. With a tube containing hydrogen at a pressure about a fraction of 1 mm. the lines lying outside the region from $\lambda 6200$ to $\lambda 5700$ were especially affected just as in the case of the addition of mercury vapour or of helium. Some of lines within this region also suffered changes in their relative intensities. (Fig. 9).

These changes are not characteristic to bromine, but are similar in nature to that produced by the addition of mercury vapour or by the increase of hydrogen pressure.

Hydrogen-Iodine, Hydrogen-Chlorine, and Hydrogen-Sulphur tubes

With these tubes many difficulties were experienced to keep the condition of discharges unaltered during exposures to the spectrograph, and many photographs taken were found to be useless for the purpose. Beside these, lines and bands of these substances lying in the region yellow to red superposed upon the lines of hydrogen spectrum, and

the comparison of intensities of lines became very difficult. But their effects upon the secondary spectrum of hydrogen seemed to be similar to that of bromine. To draw a conclusion further studies are necessary.

All the above results revealed that the influence on a secondary spectrum of hydrogen at a low pressure of the addition of the vapour of an electro-positive element such as mercury is similar in nature to that of the vapour of an electro-negative element as bromine, and that such a change is also produced by raising simply the pressure of hydrogen. Comparing these results with the one obtained by Merton, the influence of the presence of helium in hydrogen is in many respects similar to that of mercury, bromine or hydrogen, but in a few lines its influence is opposite to those of the other vapours. Whether this difference is due to the difference in relative amounts of hydrogen and the external gas added, or this is caused by the specific action of helium remains unsolved by this experiment. But it will be certain that the secondary spectrum consists of groups of lines whose behaviours under different physical conditions are not equal. Fulcher classified the spectrum into two groups by comparing the low and high potential discharge spectra, and Merton divided it by observing the change in intensity of lines produced when a sufficient amount of helium was added. In our experiment, the grouping was done by studying the change in intensity when hydrogen, mercury and bromine vapours were added separately to hydrogen at a low pressure.

The results obtained by these different experiments did not give exactly the same groupings of lines, but in many respects they have some common points. The very complex character of the secondary spectrum will thus be reduced into a somewhat simpler one.

The two groups of lines mentioned above would perhaps be due to certain different mechanisms in hydrogen molecules. If we follow the idea that the secondary spectrum of hydrogen is emitted from its molecules during the process of recombination, two different ways of recombination should be considered. Generally the formation of a neutral molecule as a result of recombination may be done in the following ways: the one is the reunion of a positively charged molecule with an electron, and the other is the associations of two dissociated atoms or atomions into a single neutral molecule. In the case of the association of two neutral atoms, electrons in the component atoms should not be describing their permanent orbits, otherwise the light would not be emitted during the process.

Now, it may be imagined that the changes of the configurations of electrons in atoms and consequently of their orbits before and after the recombinations considered above, will give rise to the emission of monochromatic lights, which perhaps constitute the secondary spectrum of hydrogen. According to this view, there should be some groups of lines fundamentally related in the secondary spectrum, and in fact, the above experiment shows the existence of such groups of lines.

Summary

1. The influence of the pressure of hydrogen upon its secondary spectrum was studied, and two groups of lines were sorted out: the one containing the lines enhanced, and the other weakened when the pressure was increased.
2. The relation of the groups of lines said above to those classified by Fulcher and Merton was discussed.
3. The influence of the addition of vapour of mercury, or bromine to hydrogen upon the intensities of the lines of the secondary spectrum was studied, and it was found that their influence are similar to that of simply raising pressure of hydrogen.
4. A consideration about the existence of groups of lines in the secondary spectrum was given.

In conclusion, the writers wish to express their thanks to Prof. T. Mizuno for the interest he has taken in this work.

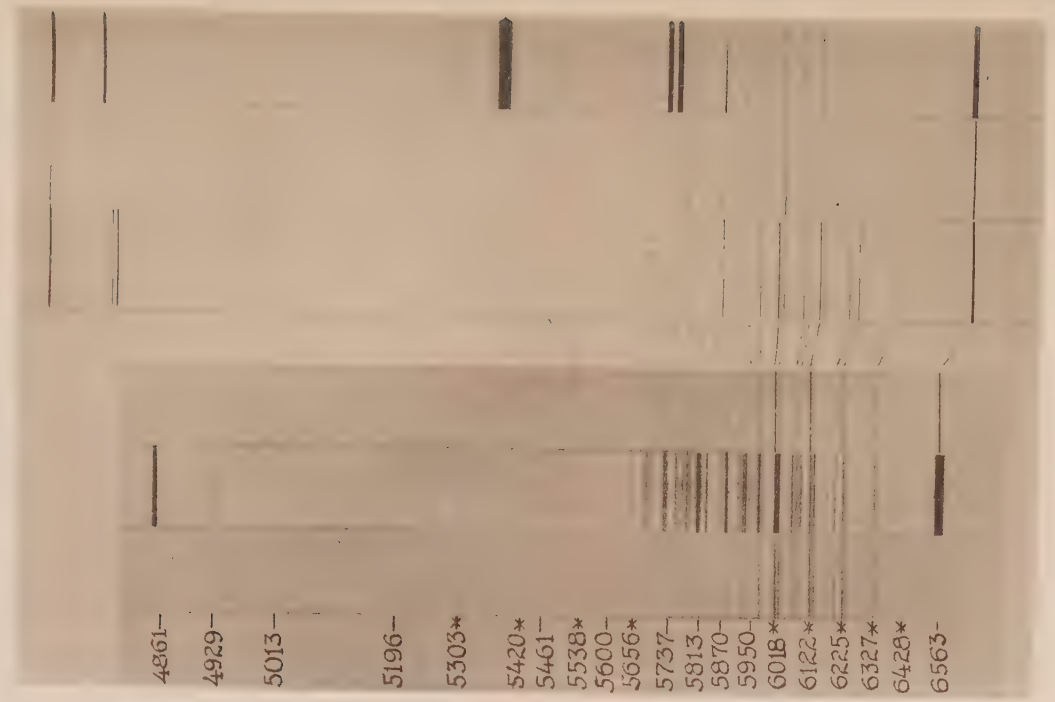


Fig. 8. Hydrogen mixed with Mercury Vapour. at a high pressure.

Fig. 4. Hydrogen at relatively high pressure.

Fig. 1. Hydrogen at low pressure.

Fig. 5. *a* 50 volts excitation.

b Geissler tube.

c 35-45 volts excitation.

Fig. 3. Hydrogen at relatlvely high pressure.

Fig. 2. Hydrogen at low pressure.

A : Hydrogen at a very low pressure.
B : Hydrogen at a relatively high pressure.

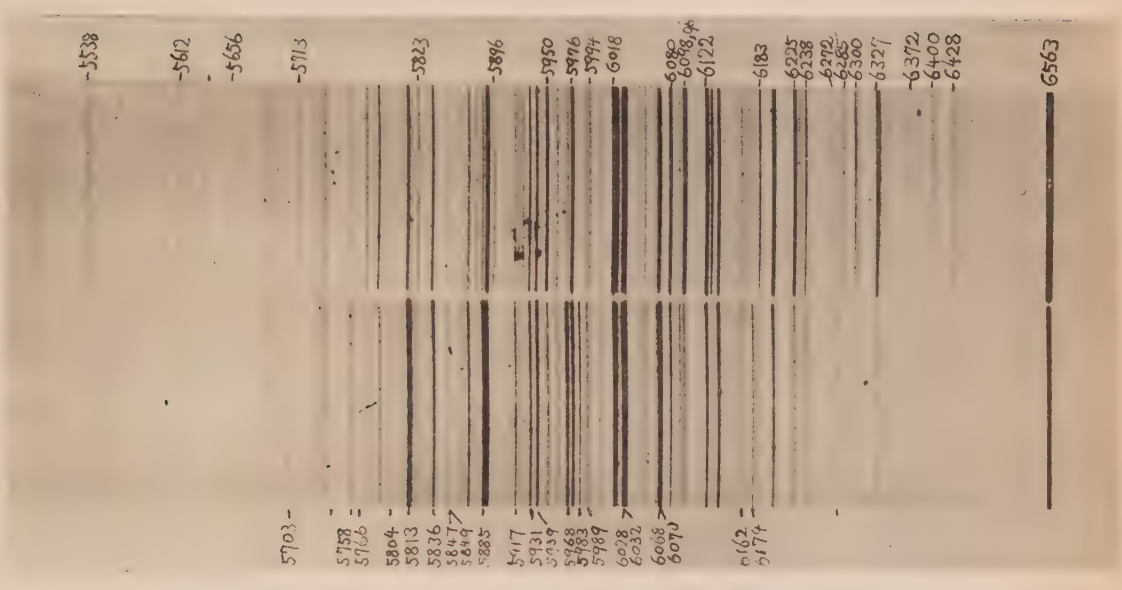
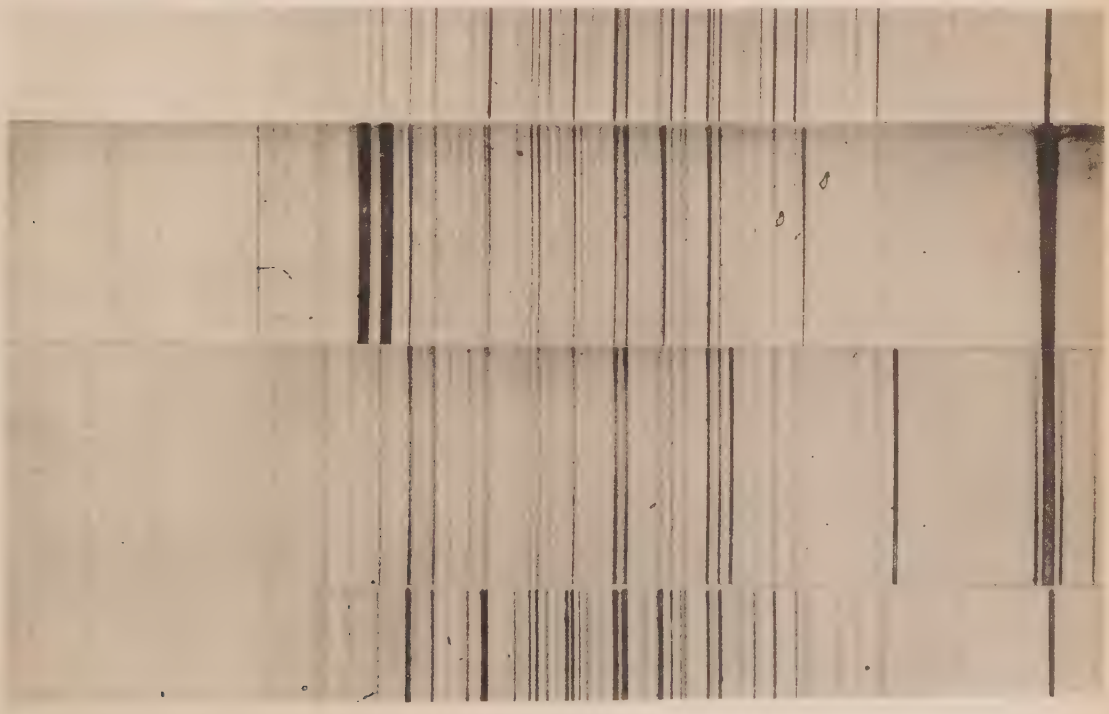


Fig. 7 : Hydrogen with Mercury vapour.
Fig. 9 : Hydrogen with Bromine vapour.
Fig. 10 : Hydrogen at a low pressure.
Fig. 11 : Hydrogen at a relatively high pressure.



A Note on the Intensities of the Lines of the Balmer Series of Hydrogen

By

Masamichi Kimura aud Mitsuharu Fukuda

(Received May 28, 1921)

In a course of the study of the iodine spectrum containing a trace of water vapour, one of us noticed that the line Hα of hydrogen was very intense in comparison with the lines of the higher member of the Balmer series. This suggested that the iodine vapour suppresses higher members of the Balmer lines and led us to the further study of the phenomena. Examining the literatures, it was found that Holtzmark[1] has studied the influence of iodine vapour upon the intensity ratio of Hβ to Hγ of the lines of the Balmer series of hydrogen. He concluded that an addition of iodine vapour to hydrogen has no appreciable influence upon the intensity ratio of these lines, when the mixture of these gases was excited by cathode rays. But the phenomena would depend upon the vapour density of iodine, and consequently the following experiments were performed to see how the behaviour of iodine vapour varies with its densities.

The spectral tubes first used in this experiment were of the form of an ordinary Geissler tube having two side tubes. In one of the tubes a piece of metallic sodium free from oil was put and a small quantity of an iodine crystal was placed in the other. The air in the tube was pumped out with a Gäde pump, and then a proper amount of hydrogen was driven out from the sodium by heating it gently with

---

[1] Ann. d. Phy. **55**, 245 (1918).

a fine jet of gas flame. The vapour density of the iodine was controlled by changing the temperature of a side tube containing it, but both the hydrogen and iodine were soon used up, and a satisfactory result was not obtained. Next, the hydrogen spectrum emitted by hydrogen iodine was photographed at various pressures, and these were compared with that of pure hydrogen at the same pressures. By such a procedure the influence of iodine vapour upon the spectrum of hydrogen can be studied.

In the study of the spectrum of hydrogen emitted from a tube containing hydrogen iodide, the gas chemically prepared was constantly passed slowly through the discharge tube, which was excited by an uncondensed discharge from an induction coil. The light emitted from the side of the capillary portion was analysed with a small spectrograph having a constant deviation prism. The spectrum was taken at the pressure of $\frac{1}{2}$, 3, 7, 10, and 14 mm. of the hydrogen iodide. The spectrum of pure hydrogen was also photographed at the corresponding pressures. For each of these pressures, the times of exposure were varied, and two plates having almost equal intensity for Hα were selected from the spectrograms of hydrogen and hydrogen iodide. By these two plates, the intensities of the remaining members of the Balmer lines were compared. The result obtained in this way is not of course quantitative. But this affords us a qualitative idea about the influence of iodine vapour upon the intensity distribution of the Balmer lines.

We now proceed to describe the result. On the spectrum emitted by the hydrogen iodide at the pressure of $\frac{1}{2}$ mm., lines of the Balmer series and the spectra of iodine appeared pretty strong, while the secondary spectrum was very faint. As the vapour pressure was raised, both the hydrogen and iodine spectra got stronger and the secondary spectrum appeared distinctly. The intensity distribution among the lines of the Balmer series emitted from such tube remained almost the same as that of pure hydrogen up to the pressure of 7 mm. But at the pressure of 10 mm. Hβ, Hγ, Hδ, etc. became distinctly less intense in the hydrogen iodide tube than in the pure hydrogen at the same pressure. This difference came out more distinctly with the spectrum taken at the higher pressure of 14 mm. (Fig. 3).

According to Holtzmark, as stated before, an addition of iodine to hydrogen has no appreciable influence upon the intensity ratio of the lines Hβ to Hγ when the mixture of these gases was excited by

cathode rays, and this intensity ratio depends upon the partial pressure of hydrogen. As regards the partial pressure of iodine in the gas mixture, he did not give an exact statement but only supposed it was very small. In our experiments, however, intensities of higher members of the Balmer lines are reduced decidedly in comparison with Hα when a certain amount of iodine vapour was added to hydrogen.

A similar experiment was also performed with chlorine. In this case, vapour of hydrogen chloride chemically prepared was passed slowly through a discharge tube, and the lights emitted from the side of the capillary at various pressures were photographed through the same spectrograph. The spectrum thus obtained was compared with that of hydrogen taken at the corresponding pressure. The result is that the lines of higher members in the former spectrum were weaker than those in the latter, the intensities of Hα being made almost equal for the both spectra. In Fig. 2, "a" shows the spectrum emitted by HCl gas at the pressure of 15 mm, "b" that of pure hydrogen at the same pressure, and "c" the spectrum emitted by a tube having NaCl-electrodes and containing a small amount of hydrogen. In these three spectrograms, the intensity of Hα from hydrogen tube is little less than those of the remaining ones, but the intensity of Hδ from the pure hydyogen is clearly stronger than the other.

Addition of vapour of sulphur, mercury (Fig. 4) or sodium separately to hydrogen gave similar results. Thus all of the results obtained tell us that the presence of a certain amount of vapour of external gas either electro-positive or electro-negative in hydrogen at a small pressure reduces the intensity of higher members of the lines of the Balmer series.

Lastly, the influence of the raise of hydrogen pressure upon the intensity distribution under consideration was studied, and the result is shown by the two spectra (Fig. 1): "a" represents hydrogen spectrum taken at a low vapour density, while "b" that of higher density. The lines Hγ and Hδ in "a" are evidently stronger than those in "b", Hα being nearly equal in the both spectra.

Merton[1] has already found that in a water vapour tube intensities of Hβ, Hγ and Hδ were reduced in comparison with those of pure hydrogen in the ratio of $\frac{1}{2}$, $\frac{1}{3}$ and $\frac{1}{4}$ respectively, while those emitted by a trace of hydrogen in helium at a high pressure were reduced

1 Proc. Roy. Soc. **96**, 112 (1920).

only to 3/4, 2/5, 1/4 and 2/13. The results are very interesting, but he did not exactly give the pressures of his tubes.

Our results show that the intensity distribution among the lines of the Balmer series is greatly affected by the pressure of hydrogen, and that the presence of a certain amount of external gases such as iodine, chlorine, mercury, etc. has much larger influence than hydrogen itself at the same pressure. The phenomena described above will partly be due to the pressure effect and partly to certain specific action of foreign atoms or atomions toward hydrogen atoms. Indeed, the fact that the higher members of the Balmer series were suppressed in the case of the present experiment might be expected if we simply accept the so-called Bohr's Theory.

Summary

1. Influence of the vapour pressure of hydrogen, and that of presence of chlorine, iodine or mercury in hydrogen tubes upon the intensities of the lines of the Balmer series were studied.
2. It was found that the presence of certain amounts of the vapours in hydrogen at a small pressure reduces selectively the intensities of higher members of the lines of the Balmer series.

In conclusion, the writers wish to express their thanks to Prof. T. Mizuno for the interest he has taken in this work.

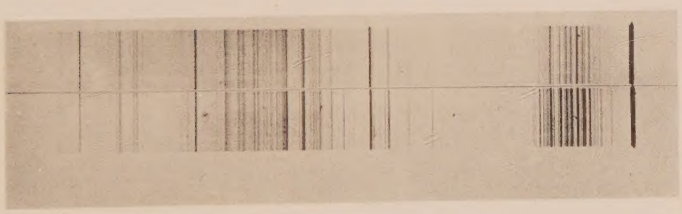
Fig. 1.

a Hydrogen: press: low
b press: high

Fig. 2.

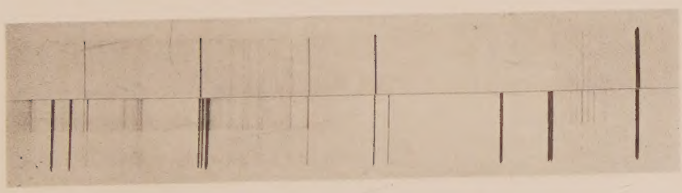
a HCl. press. 15 mm.
b H_2 press 15 mm.
c H_2 in chlorine tube.

Fig. 3.



Hydrogen.
Hydrogen iodide.

Fig. 4.



Hydrogen.
Hydrogen with Mercury.

Vol. V, No. 2, Published December 10th, 1921.

Price - - - Yen 2.00

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO, YOKOHAMA, FUKUOKA & SENDAI.

大正十年十二月七日印刷

大正十年十二月十日發行

編纂兼發行者　京都帝國大學理學部

印刷者　大久保秀次郎

東京府下北豊島郡巣鴨町三丁目十番地

印刷所　株式會社 東京築地活版製造所

東京市京橋區築地二丁目十七番地

賣捌所　丸善株式會社

東京、大阪、京都、横濱、福岡、仙臺

CONTENTS.

The Spark Potential Difference between Spheres.
By Usaburo Yoshida 97

Electrolytic Reactions of Naphthalene and its Derivatives. Part I. Electrolytic Oxidation of Naphthalene.
By Kashichi Ono 111

On the Solubility of Calcium Carbonate in Water in Equilibrium with a Gaseous Phase containing Carbon Dioxide.
By Yukichi Osaka 131

The Spectrum of the Luminosity of the Brush and the Glow Discharges of Electricity.
By Usaburo Yoshida and Hideki Hirata 143

The Secondary and the Tertiary Figures produced on Photographic Plates by Electric Discharges.
By Usaburo Yoshida and Shinsuke Tanaka 145

Influences of the Presence of Gases or Vapours upon the Intensities of the Lines of the Secondary Spectrum of Hydrogen.
By Masamichi Kimura and Mitsuharu Fukuda 153

A Note on the Intensities of the Lines of the Balmer Series of Hydrogen.
By Masamichi Kimura and Mitsuharu Fukuda 165